Sveriges lantbruksuniversitet
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Removal Efficiency of Perfluoroalkyl Substances (PFASs) in Drinking Water

– Evaluation of granular activated carbon (GAC) and anion exchange (AE) using column tests, and the effect of dissolved organic carbon

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Department of Aquatic Sciences and Assessment
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Abstract

Poly- and perfluoroalkyl substances (PFASs) are a group of environmental contaminants that have gained increasing attention due to their potential to bioaccumulate, environmental persistence and potential toxicity. PFASs have been found in surface water, sediment, air, soil, sludge and ice caps globally, as well as in wildlife and humans. Furthermore, PFASs have also been detected in drinking water, leading to raised concerns for human health, since drinking water is one of the most significant sources of PFASs for the general population. Conventional water treatment techniques have shown to be ineffective removing PFASs, highlighting the importance for further research to develop efficient removal techniques.

The aim of this study was to investigate the removal efficiency of PFASs in water using two treatment techniques; granular activated carbon (GAC), type Filtrasorb 400®, and anion exchange (AE), type Purolite A-600. Additionally, the effect of dissolved organic carbon (DOC) on removal efficiency was studied. The removal efficiency of PFASs was studied in pilot-scale column experiments at Bäcklösa drinking water treatment plant (DWTP) in Uppsala, Sweden. The laboratory batch experiments were performed at Swedish University of Agricultural Sciences (SLU), Uppsala.

The results from the column experiment indicated a decrease in removal efficiency with increasing number of bed volumes (BVs) for both GAC and AE. The average removal efficiency of all PFASs (n=14) during the 140 day column study was 65% for both GAC and AE. At the end of the column experiment, the average removal efficiency of all PFASs was 49% for GAC and 53% for AE. Removal efficiency was influenced by functional group; perfluoroalkane (-alkyl) sulfonic acids (PFSAs) were more efficiently removed than perfluoroalkyl carboxylic acids (PFCAs) (on average 56% vs 38% for GAC, respectively, and 82% vs 28% for AE, respectively). In addition, the perfluorocarbon chain length influenced the removal efficiency. Results from the column experiment indicated higher removal efficiency as the perfluorocarbon chain length increased. In contrast, the results from the batch experiments indicated the opposite; decreasing adsorption to GAC and AE as the chain length increased. Furthermore, presence of DOC in the water affected the removal efficiency of the investigated PFASs. However, the results indicated, contrary to the few studies previously performed on DOC and removal efficiency of PFASs, enhanced sorption of PFASs to GAC with increasing DOC concentration, and decreased PFAS sorption to AE as the DOC concentration increased. In addition, the removal efficiency of GAC and AE varied using water types with different DOC origin, indicating that DOC characteristics influence the removal efficiency of PFASs in water.

Keywords: PFASs, perfluoroalkyl substances, removal efficiency, granular activated carbon, GAC, anion exchange, AE, dissolved organic carbon, DOC

Sammanfattning

Poly- och perfluorerade alkylsubstanser (PFAS) är en grupp syntetiska föroreningar som fått ökad uppmärksamhet på grund av deras potential att bioackumulera, persistens och potentiell toxicitet. PFAS förekommer globalt i ytvatten, sediment, luft, jord, slam, iskärnor, djur och människor. Dessutom har PFAS detekterats i dricksvatten, vilket har lett till ökad oro för människors hälsa, då dricksvatten är en av de viktigaste exponeringskällorna. Konventionella vattenreningstekniker är inte effektiva för PFAS, vilket understryker vikten av att utveckla kostnadseffektiva reningstekniker.

Syftet med denna studie var att undersöka reningseffektiviteten av PFAS i vatten genom att använda två reningstekniker: granulärt aktiverat kol (GAC), av typ Filtrasorb 400®, samt anjonbyte (AE), av typ Purolite A-600. Ett ytterligare syfte var att undersöka effekten av löst organiskt kol (DOC) på reningseffektiviteten. Reningseffektiviteten av PFAS studerades i en pilotanläggning med kolonnstudier på Bäcklösa vattenreningsverk (DWTP) i Uppsala. Dessutom utfördes bägarexperiment på Sveriges lantbruksuniversitet (SLU), Uppsala.

Resultaten från kolonnstudien indikerar minskad reningseffektivitet med ökad mängd bäddvolym för både GAC och AE. Den genomsnittliga reningseffektiviteten för samtliga undersökta PFAS (n=14) var under den 140 dagar långa kolonnstudien 65 % för både GAC och AE. I slutet av kolonnstudien var den genomsnittliga reningseffektiviteten av samtliga PFAS 49 % för GAC och 53 % för AE. Reningseffektiviteten var beroende av funktionell grupp; perfluorerade alkylsulfonater (PFSA) avlägsnades mer effektivt än perfluorerade alkylkarboxylater (PFCA) (i genomsnitt 56 % mot 38 % för GAC och 82 % mot 28 % för AE). Även den perfluorerade kolkedjans längd tycks inverka på reningseffektiviteten, då resultatet från kolonnstudien indikerar ökad reningseffektivitet med längre perfluorerad kolkedja. Resultatet från bägarexperimenten visade dock det motsatta; minskad adsorption till GAC och AE med ökad kolkedjelängd. Dessutom påverkades reningseffektiviteten av förekomsten av DOC. I motsats till tidigare studier som behandlat interaktionen mellan DOC och reningseffektivitet av PFAS visade denna studie en ökad adsorption av PFAS till GAC med ökad DOC-koncentration samt en minskad adsorption av PFAS till AE med ökad DOC-koncentration. Därtill varierade reningseffektiviteten hos GAC och AE när vattentyper med olika källor av DOC användes, vilket indikerar att karaktären hos DOC påverkar reningseffektiviteten av PFAS i vatten.

Nyckelord: PFAS, perfluorerade alkylsubstanser, reningseffektivitet, granulärt aktiverat kol, GAC, anjonbyte, AE, löst organiskt kol, DOC

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Populärvetenskaplig sammanfattning

Poly- och perfluorerade alkylsubstanser (PFAS) är en grupp mänskligt producerade ämnen som består av en funktionell grupp och en kolkedja där väteatomer helt eller delvis är ersatta med fluoratomer. Den funktionella gruppen är vattenlöslig medan den perfluorerade kolkedjan är fettlöslig, vilket leder till att PFAS har ytaktiva egenskaper (de är så kallade surfaktanter), och detta i kombination med att PFAS är väldigt stabila molekyler har lett till att dessa ämnen sedan 1950-talet använts som tillsatser och ytskikt i många varor och produkter, såsom förpackningar, brandsläckningsskum och impregneringsmedel. På senare tid har dessa ämnen även fått ökad uppmärksamhet på grund av deras tendens att ackumuleras i levande organismer, att de är långlivade i miljön och för att exponering kan medföra hälsorisker, som exempelvis njur- och testikelcancer. PFAS förekommer globalt i ytvatten, sediment, luft, jord, slam, iskärnor, djur och människor. PFAS har även detekterats i dricksvatten, vilket har lett till en ökad oro för mänsklig hälsa, då dricksvatten är en av de viktigaste exponeringskällorna för PFAS. Vattenreningstekniker som vanligtvis används inom dricksvattenrening har visat sig vara ineffektiva för PFAS, vilket visar att det finns ett behov av forskning för att utveckla kostnadseffektiva tekniker för rening av PFAS.

I den här studien undersöktes hur effektivt PFAS kan renas bort från dricksvatten med hjälp av två reningstekniker: granulärt aktiverat kol (GAC) och anjonbyte (AE). Båda teknikerna verkar genom adsorption, då PFAS adsorberas på aktiva kolets yta eller genom jonbyte på anjonbytaren, där negativa joner adsorberas på jonbytarens positiva yta. Få studier har gjorts för att undersöka hur organiskt kol i vattnet kan påverka effektiviteten hos GAC och AE, så därför undersöktes även hur löst organiskt kol (DOC) påverkar effektiviteten av reningen. Två experiment utfördes: en kolonnstudie på Bäcklösa dricksvattenreningsverk i Uppsala och ett bägarexperiment på SLU.

Studien visade att både GAC och AE kan rena dricksvattnet från PFAS, men med olika effektivitet. PFAS med en sulfonatgrupp som funktionell grupp renades bort mer effektivt än PFAS med en karboxylatgrupp. I kolonnstudien renades även PFAS med längre perfluorerad kolkedja bort mer effektivt i jämförelse med PFAS med kortare perfluorerad kolkedja; ju längre perfluorerad kolkedja desto effektivare rening. Bägarexperimenten visade däremot motsatt resultat; med längre perfluorerad kolkedja minskade reningseffektiviteten. Dessa experiment visade även att reningseffektiviteten hos GAC ökade med ökad koncentration av DOC i vattnet. För AE var det tvärtom, det vill säga minskad reningseffektivitet med ökad koncentration av DOC. Dessutom varierade resultatet beroende på vilken typ av sjövatten som användes i experimentet, vilket tyder på att olika typer av DOC påverkar reningen på olika sätt.

Kolonnstudien visade att reningseffektiviteten hos GAC och AE var lägst för PFAS med kortare perfluorerad kolkedja (mellan tre och sex kol i kedjan). Den utfasning av PFAS med längre perfluorerade kolkedjor som nu äger rum leder ofta till att de ersätts med PFAS med kortare perfluorerade kolkedjor. Detta innebär att vidare forskning som fokuserar på att rena bort PFAS med kortare perfluorerade kolkedjor är nödvändig.

Table of Contents

Abbreviations

6:2 FTSA	6:2 fluorotelomer sulfonate
AE	Anion exchange
AFFF	Aqueous film-forming foam
BV	Bed volume
BW	Body weight
C	Concentration in samples collected at the end of the experiment
C_0	Initial concentration in the water
DOC	Dissolved organic carbon
DWTP	Drinking water treatment plant
EBCT	Empty bed contact time
EFSA	European Food Safety Authority
FOSAA	Perfluorooctanesulfonamidoacetic acid
FOSA	Perfluorooctanesulfonamide
FOSE	Perfluorooctanesulfonamidoethanol
f_r	Flow rate
FTSA	Fluorotelomer sulfonate
GAC	Granular activated carbon
IS	Internal standard
K_{oc}	Soil organic carbon-water partitioning constant
MW	Molecular weight
N-EtFOSA	N-ethylperfluorooctanesulfonamide
N-EtFOSAA	N-ethylperfluorooctanesulfonamidoacetic acid
N-EtFOSE	N-ethylperfluorooctanesulfonamidoethanol
N-MeFOSA	N-methylperfluorooctansulfonamide
N-MeFOSAA	N-methylperfluorooctanesulfonamidoacetic acid
N-MeFOSE	N-methylperfluorooctanesulfonamidoethanol
NOM	Natural organic matter
PAC	Powdered activated carbon
PFAA	Perfluoroalkyl acid
PFAS	Poly- and perfluoroalkyl substance
PFBA	Perfluorobutanoate
PFBS	Perfluorobutane sulfonate
PFCA	Perfluoroalkyl carboxylic acid
PFDA	Perfluorodecanoate
PFDoDA	Perfluorododecanoate
PFDS	Perfluorodecane sulfonate
PFHpA	Perfluoroheptanoate
PFHxA	Perfluorohexanoate
PFHxDA	Perfluorohexadecanoate
PFHxS	Perfluorohexane sulfonate
PFNA	Perfluorononanoate
PFOA	Perfluorooctanoate
PFOcDA	Perfluorooctadecanoate
PFOS	Perfluorooctane sulfonate
PFPeA	Perfluoropentanoate
PFSA	Perfluoroalkane (-alkyl) sulfonic acid
PFTeDA	Perfluorotetradecanoate
PFTriDA	Perfluorotridecanoate
PFUnDA	Perfluoroundecanoate
pK_a	Acid dissociation constant
POP	Persistent organic pollutant

SPE	Solid phase extraction
S_w	Water solubility
TDI	Tolerable daily intake
V_a	Volume of adsorbent
WWTP	Wastewater treatment plant

1 Introduction

Poly- and perfluoroalkyl substances (PFASs) are widespread environmental contaminants, known to bioaccumulate through the food chain, be persistent and potentially toxic, leading to raised concerns whether PFASs can have potentially adverse effects on human health and biota (Giesy and Kannan, 2001; Martin et al., 2003; Lau et al., 2007; Rahman et al., 2014).

PFASs consist of a functional group and a carbon chain, in which several or all hydrogen atoms have been replaced with fluor atoms (Bhhatarai and Gramatica, 2010; Buck et al., 2011). The highly polar and strong carbon-fluorine bonds contributes to the extremely high thermal and chemical stability of PFASs (Rahman et al., 2014). Due to their unique properties, PFASs are used in a variety of products, such as water repellants, food packaging and several industrial processes (Prevedouros et al., 2005). Environmental emissions of PFASs mainly originates from direct release of these substances during manufacturing and use of products containing PFASs (Lau et al., 2007; Buck et al., 2011). In addition, the compounds can also be formed indirectly by abiotic and biotic degradation of precursor substances (Ahrens, 2011; Buck et al., 2011).

As a result of the stable properties and environmental emissions, PFASs have been found in a wide range of environmental matrixes globally, such as water, sediment, soil, air and biota (Lau et al., 2007). Recently, PFASs have also been detected in drinking water in several European countries and in USA (Ericson et al., 2009; Post et al., 2009; Ullah et al., 2011). Since one of the most significant sources of PFASs to the general population is drinking water (D'Hollander et al., 2010), different water treatment techniques have been applied and evaluated as an attempt to reduce the PFAS levels (Quiñones and Snyder, 2009; Post et al., 2012; Appleman et al., 2014). A number of commercially used treatment techniques, such as filtration, chlorination, coagulation and flocculation, have shown to be ineffective in the removal of PFASs from drinking water (Quiñones and Snyder, 2009; Post et al., 2012). On the other hand, other techniques, such as granular activated carbon (GAC) and anion exchange (AE), have higher removal efficiencies for PFASs (Appleman et al., 2014). However, PFASs differ in their physicochemical properties, due to different functional groups and carbon chain length (Eschauzier et al., 2012; Appleman et al., 2014; Du et al., 2014), and thus more research is needed to determine the fate of different PFASs using these techniques. In addition, many studies on PFAS removal are conducted in the absence of dissolved organic carbon (DOC), which is believed to be a significant factor influencing the removal efficiency (Rahman et al., 2014). Thus, more research is also needed to improve the knowledge of the effect of DOC on the removal of PFASs.

1.1 Objectives and hypotheses

The overall aim of this study was to investigate the removal efficiency of PFASs in water using two different treatment techniques; GAC and AE, and the effect of DOC on the removal efficiency of PFASs. The removal efficiency of PFASs was studied using column experiments at Uppsala Vatten och Avfall AB´s facility Bäcklösa drinking water treatment plant (DWTP) in Uppsala, Sweden. The interactions between PFASs and DOC were studied in laboratory scale batch experiments.

The following hypotheses were investigated in this study:

- The removal efficiency of PFASs depends on the functional group and carbon chain length.
- The presence of DOC in the water affects the removal efficiency of PFASs.

This study was not performed to optimize the two investigated treatment techniques, but rather to study their removal efficiency of the selected PFASs. The study was limited to 26 PFASs in the column experiment and 14 PFASs in the batch experiment. The treatment techniques were limited to Filtrasorb 400® (GAC) and Purolite A-600 (AE). Water from Bäcklösa DWTP was used during the column experiment, while water from lake Bolmen and lake Görväln was used in the batch experiments. Spiking solutions, with known concentrations of PFASs, were added to the water to obtain concentrations ranging between ng L^{-1} and μg L^{-1}.

2 Background

2.1 Poly- and perfluoroalkyl substances (PFASs)

PFASs are a group of aliphatic and organic compounds with the general structure of at least one carbon chain and a functional group. Within the carbon chain, several or all hydrogen atoms have been replaced with fluor atoms, according to the perfluoroalkyl moiety C_nF_{2n+1}-R, where n is the number of carbons and R is the functional group (Buck et al., 2011). If the hydrogen atoms partly have been replaced with fluor atoms, the compound is polyfluorinated. If, however, all hydrogen atoms are replaced with fluor atoms, the compound is perfluorinated (Buck et al., 2011; Livsmedelsverket, 2013). Polyfluoroalkyl substances can be degraded into perfluoroalkyl substances, both abiotically and biotically (Buck et al., 2011).

PFASs can be divided into subclasses, characterized by the functional group. The class containing the compounds mainly discussed in published literature are the perfluoroalkyl acids (PFAAs). Among the PFAAs are the perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane (-alkyl) sulfonic acids (PFSAs). PFCAs are characterized by their carboxylic group (-COOH). Among the PFCAs, perfluoro-octanoate (PFOA) is the most frequently discussed (Figure 1). PFSAs, on the other hand, are characterized by a sulfonic group ($-SO_3H$), and among the PFSAs, perfluoro-octane sulfonate (PFOS) is the most well-known (Figure 1) (Buck et al., 2011). Other important classes of PFASs are perfluorooctanesulfonamides (FOSAs), perfluorooctane-sulfonamidoethanols (FOSEs), perfluorooctanesulfonamidoacetic acids (FOSAAs), and fluorotelomer sulfonates (FTSAs), which can degrade into PFCAs and PFSAs (Buck et al., 2011).

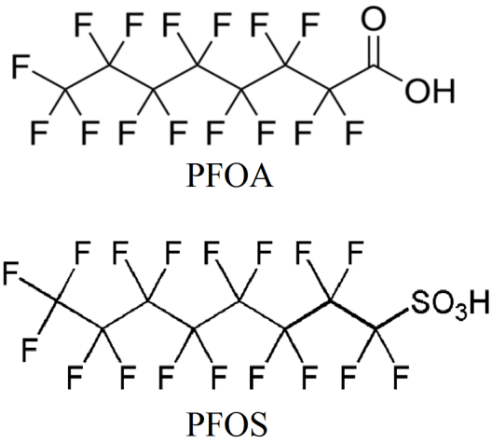

Figure 1. Chemical structure of PFOA and PFOS.

The length of the carbon chain varies between different PFASs, and is either termed short-chained or long-chained. Buck et al. (2011) proposed a terminology scheme for PFAAs, were PFSAs containing ≥6 carbons and PFCAs with ≥8 carbons are defined as long-chained. As the chain length of PFSAs and PFCAs increase, so does the bioaccumulation factor, resulting in a higher potential for long-chained PFSAs and PFCAs to bioaccumulate compared to their short-chained equivalents (Martin et al., 2003). PFCAs and PFSAs are persistent and not degraded by typical environmental degradation processes, partly due to the highly polar and strong carbon-fluorine bonds resulting in extremely high chemical and thermal stability (Rahman et al., 2014).

2.2 Physicochemical properties

PFASs comprise of both a water-soluble hydrophilic part, the functional group, and a water-insoluble hydrophobic part, the carbon chain, which is either linear or branched (Bhhatarai and Gramatica, 2010; Buck et al., 2011). As the chain length of the PFAS increases, the water solubility decreases (Bhhatarai and Gramatica, 2010). In addition, the

presence of a charged functional group affects the water solubility. PFCAs and PFSAs generally carry a charged functional group and therefore have higher water solubility than protonated PFASs with an uncharged functional group, e.g FOSAs (Ahrens, 2011).

Depending on pH value in the surrounding matrix and the acid dissociation constant (pKa), PFASs with acidic properties may be present in a protonated or an anionic form, or a mixture of both (Buck et al., 2011). Since PFCAs and PFSAs are strong acids, these substances will mainly be present in their dissociated, anionic form at environmentally relevant pH values (Rayne and Forest, 2009; Rahman et al., 2014).

In a sorption study, Ahrens et al. (2010) studied the distribution of PFASs in water, suspended particulate matter and sediment. Short-chain PFCAs (C<7) were exclusively detected in the dissolved phase, while long-chain PFCAs (C_{7-11}), PFOS, FOSA and perfluorohexane sulfonate (PFHxS) were detected both in the dissolved phase and bound to suspended particulate matter. Long-chain PFCAs (C>11) and perfluorodecane sulfonate (PFDS) were exclusively detected in sediments (Ahrens et al., 2010). Similar results were observed in a study performed by Higgins and Luthy (2006), demonstrating increased log K_{oc} values with increased carbon chain length, i.e. higher sorption potential of longer chain PFASs than their short-chained equivalents. An overview of the physical properties of the PFASs investigated in this study is presented in table 1.

Table 1. Physical properties of the studied PFASs (n=26); molecular weight (MW), water solubility (S_w), acid dissociation constant (pKa) and sorption (log K_{oc})

Substance	Acronym	Molecular formula	MW (g mol^{-1})	log Sw (mol L^{-1})	pKa	log K_{oc}
PFCAs						
Perfluorobutanoate	PFBA	$C_3F_7CO_2^-$	213.04	0.42[c]	0.4[b] 0.85[c] 0.05[e]	n.a.
Perfluoropentanoate	PFPeA	$C_4F_9CO_2^-$	263.05	-0.37[c]	0.81[c] -0.10[e]	n.a.
Perfluorohexanoate	PFHxA	$C_5F_{11}CO_2^-$	313.06	-1.16[c]	-0.16[b] 0.84[c]	1.91[f]
Perfluoroheptanoate	PFHpA	$C_6F_{13}CO_2^-$	363.07	-1.94[c]	-0.19[a] 0.82[c]	2.19[f]
Perfluorooctanoate	PFOA	$C_7F_{15}CO_2^-$	413.08	-2.73[c]	-0.20[b] 0.90[c]	2.06[d] 2.31[f]
Perfluorononanoate	PFNA	$C_8F_{17}CO_2^-$	463.09	-3.55[c]	0.82[c]	2.39[d] 2.33[f]
Perfluorodecanoate	PFDA	$C_9F_{19}CO_2^-$	513.10	-4.31[c]	-0.21[a]	2.76[d] 3.17[f]
Perfluoroundecanoate	PFUnDA	$C_{10}F_{21}CO_2^-$	563.11	-5.13[c]	-0.21[a]	3.30[d]
Perfluorododecanoate	PFDoDA	$C_{11}F_{23}CO_2^-$	613.12	-5.94[c]	-0.21[a]	n.a.
Perfluorotridecanoate	PFTriDA	$C_{12}F_{25}CO_2^-$	663.13	-6.59[c]	-0.22[e]	n.a.
Perfluorotetradecanoate	PFTeDA	$C_{13}F_{27}CO_2^-$	713.14	-7.42[c]	-0.21[a]	n.a.
Perfluorohexadecanoate	PFHxDA	$C_{15}F_{31}CO_2^-$	813.16	n.a.	-0.22[e]	n.a.
Perfluorooctadecanoate	PFOcDA	$C_{17}F_{35}CO_2^-$	913.18	n.a.	-0.22[e]	n.a.
PFSAs						
Perfluorobutane sulfonate	PFBS	$C_4F_9SO_3^-$	299.05	-1.00[c]	0.14[b,e] -3.94[c]	n.a.
Perfluorohexane sulfonate	PFHxS	$C_6F_{13}SO_3^-$	399.07	-2.24[c]	0.14[b] -3.45[c]	2.70[f]
Perfluorooctane sulfonate	PFOS	$C_8F_{17}SO_3^-$	499.09	-3.92[c]	-3.27[b] -3.41[c] 0.14[a,e]	2.57[d] 3.34[f]
Perfluorodecane sulfonate	PFDS	$C_{10}F_{21}SO_3^-$	599.11	-5.39[c]	-2.86[c] 0.14[e]	3.53[d]
FOSAs						
Perfluorooctanesulfonamide	FOSA	$C_8F_{17}SO_2NH_2$	499.12	-5.05[c]	6.56[e]	n.a.
N-methylperfluoro-octanesulfonamide	N-MeFOSA	$C_8F_{17}SO_2N(CH_3)H$	513.14	-6.35[c]	7.69[e]	n.a.
N-ethylperfluoro-octanesulfonamide	N-EtFOSA	$C_8F_{17}SO_2N(CH_2CH_3)H$	527.17	-6.97[c]	7.91[e]	n.a.
FOSEs						
N-methylperfluoro-octanesulfonamidoethanol	N-MeFOSE	$C_8F_{17}SO_2N(CH_3)CH_2CH_2OH$	557.19	-6.22[c]	14.4[e]	n.a.
N-ethylperfluoro-octanesulfonamidoethanol	N-EtFOSE	$C_8F_{17}SO_2N(C_2H_5)CH_2CH_2OH$	571.22	-6.73[c]	14.4[e]	n.a.
FOSAAs						
Perfluorooctane-sulfonamidoacetic acid	FOSAA	$C_8F_{17}SO_2N(CH_2CO_2H)H$	557.15	n.a.	n.a.	n.a.
N-methylperfluorooctane-sulfonamidoacetic acid	N-MeFOSAA	$C_8F_{17}SO_2N(CH3)CH_2CO_2H$	571.18	n.a.	n.a.	3.11[d]
N-ethylperfluorooctane-sulfonamidoacetic acid	N-EtFOSAA	$C_8F_{17}SO_2N(C_2H_5)CH_2CO_2H$	585.20	n.a.	n.a.	3.23[d]
FTSAs						
6:2 fluorotelomer sulfonate	6:2 FTSA	$C_8H_4F_{13}SO_3H$	428.13	n.a.	n.a.	n.a.

[a]Steinle-Darling and Reinhard (2008), [b]Du et al. (2014), [c]Wang et al. (2011), [d]Higgins and Luthy (2006), [e]Ahrens et al. (2012), [f]Sepulvado et al. (2011), n.a. not available

2.3 Use and regulations

The properties of PFASs, with a hydrophobic carbon chain and a hydrophilic functional group in combination with stable fluorine-carbon bonds, renders some unique chemical and physical characteristics, such as thermal and chemical stability, water and oil repellency and surfactant properties (Bhhatarai and Gramatica, 2010; Lindstrom et al., 2011). PFASs with a carbon chain length >2 carbons are considered man-made substances (Ahrens, 2011), and are manufactured using mainly two processes; electrochemical fluorination and telomerization (Buck et al., 2011). However, vulcanic activity is also a potential source of longer chained PFASs to the atmosphere (Ahrens, 2011). Since the 1950´s, PFASs have been used within a wide range of both industrial and commercial application areas including lubricants, fire-fighting foams, food packaging and as water repellants in leather, textile and paper (Prevedouros et al., 2005; Järnberg et al., 2006).

Within the project 2010/2015 PFOA Stewardship Program, starting in 2006, the US Environmental Protection Agency cooperates with eight leading chemical companies to reduce the emissions of PFOA and long-chained PFASs with 95% by 2010, and aim for total elimination of emissions of long-chain PFASs by the end of 2015 (US Environmental Protection Agency, 2006). A similar agreement has been concluded in Canada, where Canadian environmental and health authorities cooperate with four companies to restrict PFCAs in their products (Environment Canada, 2010). Within the European Union, PFOS and PFOS-related compounds (precursor compounds that can degrade into PFOS) have been banned to use in chemical products and articles since 2008 (European Parliament, 2006). In May 2009, PFOS was included in Annex B of the Stockholm Convention on Persistent Organic Pollutants (POPs), resulting in restrictions in production and use in the countries agreeing to the convention (UN Environmental Programme, 2009). In addition, PFOS and PFOS-related compounds were included in the Convention on Long-Range Transboundary Air Pollution (CLRTAP) in 2009 (United Nations Economic Commission for Europe, 2009).

Phase-out of PFOS, PFOA and related substances results in replacement with (most often) shorter chained PFASs, such as PFBS, which are considered to be less bioaccumulative. However, knowledge on potential adverse effects of the substitutes are still limited (Wang et al., 2009). In addition, manufacturing and use of the regulated PFASs, such as PFOS and PFOA, may shift to countries that are not part of these agreements (Lindstrom et al., 2011).

2.4 Occurrence and fate

The global distribution of PFASs in wildlife and humans was first discovered in the early 2000´s. Giesy and Kannan (2001) studied the distribution of four PFASs in urbanized locations in North America and Europe, as well as more remote locations such as the North Pacific Ocean and the Arctic. The results showed that PFOS was widespread in the environment, however with higher levels in animals living in or close to urbanized areas compared to animals living in remote areas. In addition, the results showed that the levels were higher in predatory animals, such as bald eagle (*Haliaeetus leucocephalus*) and mink (*Neovison vison*), than in their prey, suggesting that PFOS is bioaccumulative (Giesy and Kannan, 2001). PFOS has also been found in human blood, blood serum and blood plasma collected globally, with the highest levels detected in samples collected in

Poland and United States (>30 ng mL^{-1}) and the lowest in India (<3 ng mL^{-1}) (Kannan et al., 2004).

Environmental emissions can occur directly during the manufacturing processes and use of products containing PFASs. An additional pathway is indirect sources, such as degrading of precursor substances (Prevedouros et al., 2005; Buck et al., 2011). PFOA, PFOS and other PFAAs have been found in several environments globally, such as surface water, ice caps, air, sludge, sediment and soil (Lau et al., 2007). When focusing on the aquatic environment, there are a number of sources. One point source of PFASs to surface waters is wastewater treatment plants (WWTPs) (Nakayama et al., 2010). WWTPs, along with landfills, are also a major point source of PFASs to the atmosphere (Ahrens et al., 2011). An additional point-source of PFASs is the use of aqueous film-forming foams (AFFFs) at e.g. fire-fighting training sites, where elevated levels of especially PFOS has been detected in adjacent surface waters (Moody et al., 2003; Järnberg et al., 2006). Lastly, industrial use of chemicals, as well as consumer use of products containing PFASs, contributes to elevated levels in the environment (Borg and Håkansson, 2012).

PFASs, particularly PFOS and PFOA, have also frequently been detected in drinking water. Ullah et al. (2011) analyzed tap water from six European universities to determine the levels of 15 PFAAs. The highest levels were found in Stockholm (PFOS, 8.8 ng L^{-1}) and Amsterdam (PFOA, 8.6 ng L^{-1} and PFBS, 18.8 ng L^{-1}), thus raising the concern for the PFOS substitute PFBS (Ullah et al., 2011). Similar results has been shown in Spain, where PFOS, PFHxS, PFHxA and PFOA were frequently detected in tap water (maximum concentrations, 58.1, 5.3, 69.4 and 57.4 ng L^{-1}, respectively) (Ericson et al., 2009) and also in New Jersey, Ohio and West Virginia, USA (Post et al., 2009; Hoffman et al., 2010). In Uppsala, a pilot study was conducted to determine levels of PFAAs in tap water collected in different districts of the city. The results indicated elevated levels of PFOS (>20 ng L^{-1}) and PFHxS (>40 ng L^{-1}) in water samples from two of the seven sampled districts (Livsmedelsverket, 2012).

During the years 1996-2010, the Swedish National Food Agency examined the levels of PFAAs in blood serum samples from primiparous women in Uppsala. The levels of PFBS and PFHxS have increased exponentially, while the levels of PFOS have decreased during the period (Figure 2) (Glynn et al., 2012; Livsmedelsverket, 2012). The downward trend in PFOS has been confirmed in other studies, and is explained by the phase-out of PFOS occurring since early 2000´s (Livsmedelsverket, 2012). The exponential increase in PFHxS is, however, not consistent with the two additional Swedish studies on exposure to PFHxS, where the levels instead have levelled off or decreased since the early 2000´s. The increase in PFHxS levels in blood serum samples in Uppsala can partly be explained by elevated levels in drinking water (Livsmedelsverket, 2012). Another possible explanation for the increase in PFBS and PFHxS levels is replacement of PFOS and PFOS-precursors with these shorter chained substances (Wang et al., 2009).

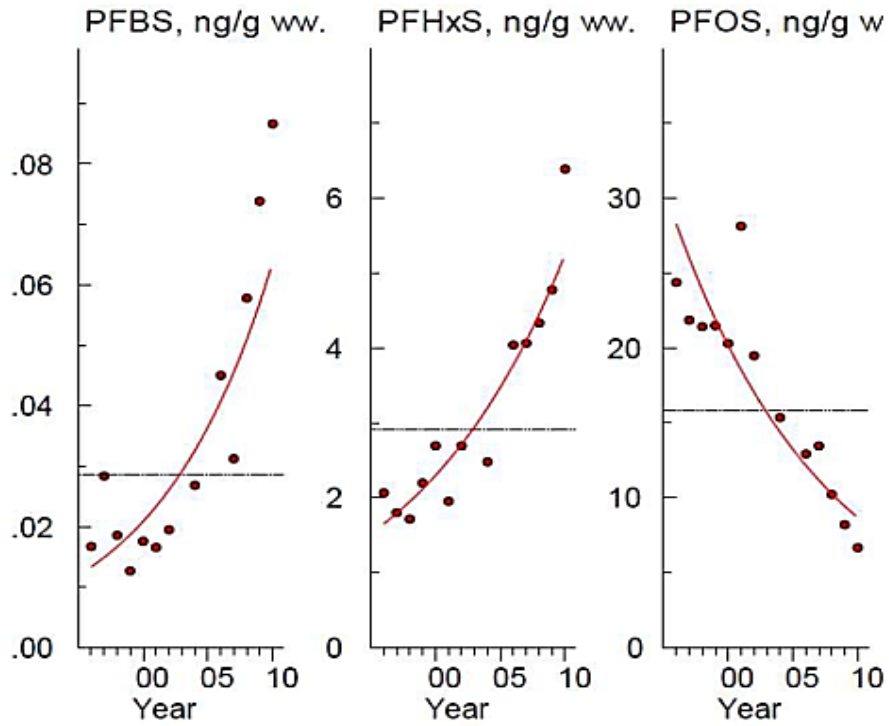

Figure 2. Temporal trends of PFBS, PFHxS and PFOS in blood serum samples collected from primiparous women in Uppsala, Sweden. Samples were collected between the years 1996-2010. From Livsmedelsverket (2012), with permission.

2.5 Toxicity

For the general population, the most significant sources of PFASs are through ingestion of food, including drinking water, and inhalation of dust (D'Hollander et al., 2010). Unlike most other POPs, PFASs are not distributed and accumulated in fatty tissues. Instead, PFASs are distributed to proteins, such as albumin, in plasma, liver and eggs and, in addition, to fatty acid binding proteins in cells (Borg and Håkansson, 2012). A number of adverse health effects have been associated with PFASs. Exposure to PFOA has been linked to kidney and testicular cancer. In addition, increased blood serum levels after exposure to PFASs, has been associated to a lower birth weight, infertility and lower than average sperm counts in young men (Rahman et al., 2014).

A risk analysis performed by the Swedish National Food Agency indicated a sufficient marginal between background intake of investigated PFAAs and risk of adverse health effects on liver and reproduction (Livsmedelsverket, 2013). The background intake of PFOS and PFOA was also marginally lower than the Tolerable Daily Intake (TDI) proposed by the European Food Safety Authority (EFSA). The, by EFSA, proposed TDI:s are for PFOS 150 ng kg BW^{-1} day^{-1} and for PFOA 1 500 ng kg BW^{-1} day^{-1}. However, recent animal studies indicate that PFOS is more immunotoxic than EFSA first suggested in 2008, resulting in a potential need for the guidelines to be revised (Livsmedelsverket, 2013). In addition, Post et al. (2012) performed an information review on PFOA sources, occurrence in drinking water, toxicokinetics and health effects, in which the authors "suggests that continued human exposure to even relatively low concentrations of PFOA in drinking water results in elevated body burdens that may increase the risk of health effects".

2.6 Interactions between PFASs and DOC

Dissolved organic carbon (DOC) is a term describing organic material of varying composition and origin present in aquatic environments. DOC can be divided into two fractions; one humic fraction which is more hydrophobic and one non-humic which is more hydrophilic (Owen et al., 1995). The humic fraction can vary between 35 and 70%, depending on origin (Machenbach, 2007). The organic components in DOC varies with origin and season; factors affecting the structure of DOC are for example topography, climate, soil type and vegetation surrounding the water (Machenbach, 2007). Another factor contributing to the DOC characteristics is the source of the organic material; whether the material is autochthonous or allochthonous. Autochthonous material is mainly hydrophilic and produced by bacteria or algae within the lake while allochthonous material is mainly hydrophobic with terrestrial origin, primarily from decomposed plant material (Fabris et al., 2008; Filella, 2009).

There is limited knowledge regarding the interactions between PFASs and DOC in drinking water. However, the sorption of PFASs to sediment has been shown to increase with increasing organic matter content (Higgins and Luthy, 2006; Ahrens et al., 2009b). A study performed by Jeon et al. (2011) suggests that hydrophobic interaction is the main driving force when PFASs are sorbed to organic matter. In addition, functional group and perfluorocarbon chain length influence the partitioning in sediment; PFSAs were found to bind more strongly to sediment compared to PFCAs, and short-chained PFCAs ($C \leq 7$) were exclusively found in pore water (Ahrens et al., 2009b).

2.7 Treatment techniques

As some PFASs have potential to cause adverse effects on human health, different treatment options have been examined to reduce the levels of PFASs in drinking water. Quiñones and Snyder (2009) studied the removal of PFAAs (e.g. PFOS, PFOA and PFHxS) using different treatment trains in full-scale water treatment systems, including filtration, ozonation, coagulation/flocculation, and chlorination processes. The study indicated that all studied combinations of treatment processes were ineffective, with no or low reduction in PFAA levels (Quiñones and Snyder, 2009). Similar results can be seen in a study performed by Appleman et al. (2014), and the authors additionally highlights the use of other treatment options, such as reverse osmosis, activated carbon and anion exchange (AE), which have been shown to decrease the PFAS levels in drinking water (Appleman et al., 2014).

2.7.1 Granular activated carbon

Adsorption is a process during which substances present in a liquid phase are adsorbed to and accumulated on a solid phase, resulting in removal from the liquid phase (Crittenden et al., 2012a). Powdered activated carbon (PAC) and granular activated carbon (GAC), produced from bituminous coal, lignite coal, coconut shells and wood, are adsorbents widely used in DWTPs for reducing compounds causing odour and taste, concentrations of organic contaminants and occasionally natural organic matter (NOM) (Rahman et al., 2014). PAC can be added during any of several steps in the treatment train, directly to the water, and is removed using filtration or sedimentation. GAC, on the other hand, is operated in fixed-beds (Crittenden et al., 2012a). Since GAC is experimentally used in this study, the focus will be on this adsorbent.

In addition to the primary application areas mentioned above, GAC has been shown to decrease the concentrations of several PFASs. During a study on the removal of PFASs in a DWTP in Amsterdam, Eschauzier et al. (2012) concluded that only GAC treatment (Norit ROW 0.8 Supra®) was efficient in removing PFASs, while the preceding treatment steps (coagulation, rapid sand filtration and ozonation) did not reduce the PFAS concentrations. During the GAC treatment, long chain PFAAs such as PFOS and PFNA were completely removed, PFOA decreased with approximately 50%, and thereafter the removal efficiency decreased as the carbon chain length decreased. Shorter chained PFASs such as PFBA, PFBS, PFPeA, PFHxA and PFHpA showed little or no reduction. The initial PFAS concentrations ranged between 0.3 to 29 ng L^{-1} and the empty bed contact time (EBCT), during which the molecules were in contact with the adsorbent, was two times 20 minutes (Eschauzier et al., 2012). In addition, Flores et al. (2013) observed partial removal of PFOS (63%) and PFOA (41%) when comparing raw water, with PFAA levels ranging between <4.2 and 35 ng L^{-1}, and GAC (Filtrasorb 400®, Norit 1240 EN® and Norit ROW 0.8®) treated water in a Spanish DWTP. No contact time was stated in the article, however, a maximum total loading of 52 m^3 H_2O kg^{-1} GAC was purified to prevent breakthrough of analytes (Flores et al., 2013).

Ochoa-Herrera and Sierra-Alvarez (2008) performed batch experiments using GAC (Filtrasorb 300® and Filtrasorb 400®) to determine the sorption of PFOS, PFOA and PFBS. The results were similar to those by Eschauzier et al. (2012), with PFOS as the strongest sorbed substance, followed by PFOA and PFBS, suggesting that carbon chain length and possibly the functional group influence the sorption. The initial PFAS concentrations ranged between 15-150 mg L^{-1} and the experiments were performed in flasks shaken for 48 hours (Ochoa-Herrera and Sierra-Alvarez, 2008). An additional batch experiment was performed by Yu et al. (2009), as an attempt to determine the sorption isotherms of PFOS and PFOA. The initial PFOS and PFOA concentrations ranged between 20 and 250 mg L^{-1}, and the experiments were performed in flasks shaken for 12 hours (PAC) and 168 hours (GAC and AE). For both PFOS and PFOA, the sorption kinetics on GAC and AE were very slow, reaching sorption equilibrium after at least 168 hours. The authors suggest that this is due to a large fraction of micropores in the adsorbents, into which it takes long time to diffuse, thus lowering the sorption velocity. For PAC, on the other hand, sorption equilibrium was reached after four hours, indicating higher sorption velocity when the particles are smaller (Yu et al., 2009).

To maintain high removal efficiency, GAC filters need to be regenerated within certain time intervals. Takagi et al. (2011) observed that filters used for PFAS removal in DWTPs during a longer period of time (>1 year) were less efficient removing PFOA and PFOS. The authors concluded that activated carbon filters should be regenerated two or three times per year. In addition, Takagi et al. (2011) occasionally detected higher PFOA and PFOS levels in GAC treated water compared to untreated water when the filters had been used for a longer period of time, indicating that desorption occurred when the filters were saturated. Eschauzier et al. (2012) also observed desorption in their study, as PFBS levels occasionally were higher after GAC treatment. According to the authors, the desorption was probably due to displacement by highly sorptive components competing for sorption sites, i.e. short chain PFAAs were replaced by longer chain PFAAs (Eschauzier et al., 2012). In addition, the removal efficiency of GAC can be reduced

during presence of organic matter, such as DOC, competing for active sites as well as preloading or fouling of the GAC (Altmann et al., 2014; Rahman et al., 2014).

2.7.2 Anion exchange

Anion exchangers (AEs) have a surface with positively charged active groups which, due to electrostatic attraction, attract ions with negative charge (anions). AE occurs when anions in the aqueous phase adsorbs to the solid material (AE matrix), and in turn previously adsorbed anions are released from the solid material into the aqueous phase, to maintain electro-neutrality. AEs can have both natural origin, such as kaolinite, or be of a synthetic material, such as a polymeric resin (Crittenden et al., 2012b). When using ion exchange technology within drinking water treatment, the primary application areas are demineralization and water softening, e.g. removing calcium, magnesium and chloride ions (Crittenden et al., 2012b). In addition, the technique is now applied as an attempt to remove PFASs. As PFAAs are anionic at environmentally relevant pH values, these substances would be expected to be potentially removed by AE. The two primary mechanisms for PFAS removal are proposed to be adsorption via hydrophobic interactions and electrostatic interactions (Rahman et al., 2014).

AE resin properties with possible effects on removal efficiency are polymer matrix, porosity and active groups (Deng et al., 2010). In a review performed by Du et al. (2014), the authors reported that previous studies indicated faster adsorption kinetics for short chain PFASs, since smaller molecules are more easily transported into porous AE resins. However, previous studies also indicated higher adsorption capacity for PFSAs and PFCAs as the carbon chain length increased, due to lower water solubility, when hydrophobic interaction is involved as an adsorption mechanism (Du et al., 2014). In addition, resin matrix affects the removal of PFASs. Deng et al. (2010) studied sorption of PFOS using six different types of resins, resulting in the highest initial sorption rate and highest sorption capacity at equilibrium using polyacrylic resins, where equilibrium was reached after 48 hours. In contrast, both macroporous polystyrene resins and gel-type polystyrene resins reached equilibrium after more than 168 hours (Deng et al., 2010). In addition, Lampert et al. (2007) performed batch experiments using wastewater with initial concentrations 4 320 mg L^{-1} and 950 mg L^{-1} for PFOA and PFOS, respectively. Six AE resins were evaluated and sampling of the batch experiments occurred after 1, 5 and 25 hours. AE resin Siemens A-714 demonstrated >99% removal efficiency of both PFOA and PFOS after 25 hours, while the lowest performing AE resin (A-244) removed 37% and 54% of PFOA and PFOS, respectively (Lampert et al., 2007). However, as most studies have been performed in the absence of DOC, further studies are needed to determine the influence of DOC on AE resins during PFAS removal (Rahman et al., 2014).

Few full-scale studies on AE and PFAS removal have been conducted. However, one study using a strongly basic AE (Purolite FerrlX A33e) in full-scale at a DWTP in New Jersey was performed by Appleman et al. (2014). Influent concentrations were at low ng L^{-1} and resulting removal efficiencies after the AE treatment were moderate to high for C_6 and C_7 PFCAs (54% for PFHpA and 76% for PFOA) and PFSAs (>90%, >97% and 83% for PFOS, PFHxS and PFBS, respectively). For shorter-chain PFCAs (PFBA, PFHxA and PFPeA) the removal was low or nonexistent. The hydraulic retention time, during which the substances were in contact with the adsorbent, was six minutes (Appleman et al., 2014).

3 Material and methods

The pilot-scale column experiment was performed at Uppsala Vatten och Avfall AB´s facility Bäcklösa DWTP in Uppsala, and the batch experiments were performed at the Swedish University of Agricultural Sciences (SLU), using water from lake Görväln and lake Bolmen. Analyses of all samples were performed at the Department of Aquatic Sciences and Assessment, SLU.

3.1 Chemicals and materials

3.1.1 Chemicals

The 26 PFASs studied were PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA, PFOcDA, PFBS, PFHxS, PFOS, PFDS, FOSA, N-MeFOSA, N-EtFOSA, N-MeFOSE, N-EtFOSE, FOSAA, N-MeFOSAA, N-EtFOSAA and 6:2 FTSA (Table 1). As drinking water from Bäcklösa DWTP was used in the pilot-scale column experiment, these samples were analyzed for all 26 PFASs, while the samples from the batch experiments were analyzed for 14 PFASs; i.e PFBA (purity 98%), PFPeA (97%), PFHxA (≤ 97%), PFHpA (99%), PFOA (96%), PFNA (97%), PFDA (98%), PFUnDA (95%), PFDoDA (95%), PFTeDA (97%), FOSA (purity not available), PFBS (98%), PFHxS (≤ 98%) and PFOS (98%), purchased from Sigma-Aldrich (Sweden). These 14 PFASs were included in the spiking solutions used both in the reservoir tank at Bäcklösa DWTP, as well as during the batch experiments performed at SLU, with a concentration of 484.1 μg mL^{-1} and 500 μg mL^{-1} for each PFAS, respectively.

The internal standard (IS) FXIS07 containing $^{13}C_4$-PFBA, $^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-PFUnDA, $^{13}C_2$-PFDoDA, $^{18}O_2$-PFHxS, $^{13}C_4$-PFOS, all with a concentration of 20 pg μL^{-1}, and $^{13}C_8$-FOSA, d_3-N-MeFOSAA, d_5-N-EtFOSAA, d_3-N-MeFOSA, d_5-N-EtFOSA, d_7-N-MeFOSE and d_9-N-EtFOSE, all with a concentration of 50 pg μL^{-1}, purchased from Wellington Laboratories (Canada), was added to all samples.

0.1% ammonium hydroxide (25%, Sigma-Aldrich, Spain) in methanol (LiChrosolv® 99.9%, Merck KGaA, Germany) and thereafter pure methanol were used to precondition the solid phase extraction (SPE) and to elute the PFASs. The buffer for extraction contained acetic acid (>99.7%, Sigma-Aldrich, Germany), ammonium acetate (≥99.0%, Sigma-Aldrich, Netherlands) and Millipore water (Millipak® Express 20, 0.22 µm filter, Merck Millipore). Methanol, described above, and acetone (Suprasolv® 99.8%, Merck KGaA, Germany) were used for cleaning of laboratory consumables and equipment. Sodium bicarbonate ($NaHCO_3$, >99.5% purity, Merck KGaA, Germany) was used as buffer solution in the batch experiments.

3.1.2 Granular activated carbon

The GAC used during the experiments was Filtrasorb 400® (Calgon Carbon Corporation, Feluy, Belgium), which is a steam activated bituminous coal that first has been pulverized and thereafter agglomerated. Properties of Filtrasorb 400® are effective size 0.55-0.75 mm, surface area 1050 m^2 g^{-1}, iodine number 1000 mg g^{-1} and trace capacity number 10 mg cm^{-3}. Filtrasorb 400® is certified with ISO9001 and main application areas are

treatment of surface and groundwater sources for production of drinking water (Calgon Carbon Corporation, 2012).

3.1.3 Anion exchange

The AE resin used was Purolite A-600 (Purolite®, Llantrisant, Wales, United Kingdom), which is a strongly basic Type I quaternary ammonium resin with a polystyrene-divinylbenzene copolymer gel matrix. The minimum total capacity is 1.4 eq L^{-1}, the average diameter is 610 ± 90 μm and the shipping weight is 704 g L^{-1} (Purolite, 2012).

3.2 Pilot-scale column experiments at Bäcklösa DWTP

At Bäcklösa DWTP, Uppsala, treated drinking water retrieved from the plant and thereafter spiked with PFASs, was stored in a 1000 L polyethylene reservoir (Icorene™, Montereau, France). To maintain a concentration of 100 ng L^{-1} for individual PFASs in the reservoir, a standard mix solution with a concentration of 484.1 μg mL^{-1} PFASs was used. Water from the reservoir was pumped (peristaltic pump, type Watson marlow 520s) at a speed of 20 rpm into two different glass columns containing GAC and AE. The flow rates in the columns were kept constant at approximately 36 mL min^{-1}. The glass columns had an inner diameter of 5.2 cm and a length of 55 cm, with a sintered glass filter (Saveen and Werner) in the bottom. The columns were filled with 100 g of GAC and AE, respectively, corresponding to 220 mL GAC and 175 mL AE resin (Figure 3; Figure A5 in Appendix E).

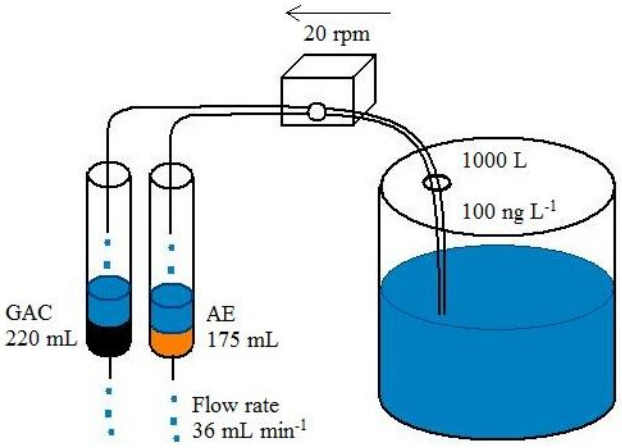

Figure 3. Illustration of the column experiment. A peristaltic pump was used to pump water from the reservoir into both columns.

Samples were collected at time points 3, 7, 11, 17, 23, 29, 35 and 42 days (Englund, 2015). In addition, samples were collected at time points 46, 56, 63, 70, 76, 84, 91, 98, 105, 112, 119, 126, 133 and 140 days during this Master thesis. At each sampling point, 1000 mL from each column and from the reservoir was collected in PP-bottles and brought to SLU for analysis. In addition, 200 mL was collected from each column and from the reservoir and standard water parameters were analyzed for samples collected at day 3 and day 48, performed by Uppsala Vatten och Avfall AB (Table A1 in Appendix A). After sample collection, the columns were backwashed for two minutes, the GAC column at a speed of 400 rpm (0.67 L min^{-1}) and the AE column at a speed of 220 rpm (0.37 L min^{-1}), using a pump (Watson marlow sci 323). Backwashing was performed to mix and redistribute the material in the columns. Finally, the reservoir was refilled and spiked.

At day 105, the GAC column was overflowing with water. As an attempt to once again increase the flow through the column, backwashing was performed for a longer period of time (4-6 minutes). However, as this treatment proved to be ineffective, backwashing was from day 119 performed using a stronger peristaltic pump (Masterflex® L/S®, easy-load 3, model 77800-62) at higher speed (600 rpm, equal to approximately 1 L min^{-1}) and for a

longer period of time (4-6 minutes). In addition, the higher flow was combined with stirring of the GAC during backwashing. After this treatment began, the water level in the column gradually decreased.

Bed volume (BV) is a unit used to normalize flow rate and volume of the adsorbent used, making the result more comparable to other studies, for example Lampert et al. (2007), Senevirathna et al. (2010) and Chularueangaksorn et al. (2013). As the flow rate or time increase, so does the number of BVs. An increased volume of adsorbent does, however, decrease the number of BVs. BV is calculated as the volume of water treated divided by the volume of the adsorbent:

$$\mathrm{BV} = \frac{f_\mathrm{r} \times t}{V_\mathrm{a}} \quad (1)$$

where f_r = flow rate (mL h^{-1})
t = time (h)
V_a = volume of adsorbent (mL)

Empty-bed contact time (EBCT) is calculated to determine the time during which the molecules are in contact with the adsorbent. An increasing EBCT results in more time during which the molecules can be adsorbed to the adsorbent (Water Treatment Guide, 2007). The EBCT is calculated as following:

$$\mathrm{EBCT} = \frac{V_\mathrm{a}}{f_\mathrm{r}} \quad (2)$$

where V_a = volume of adsorbent (mL)
f_r = flow rate (mL min^{-1})

The removal efficiency was calculated as follows:

$$\text{Removal efficiency (\%)} = 100 - \frac{C}{C_0} \times 100 \quad (3)$$

where C = concentration in samples collected after GAC or AE treatment (ng L^{-1})
C_0 = initial concentration in the reservoir tank (ng L^{-1})

3.3 Batch experiments at SLU

Water from lake Görväln was collected the 9th of March 2015, prior intake into the DWTP (GPS coordinates 6589768, 655916, SWEREF99 TM) and is hence raw water from a depth of 22 meters. Water from lake Bolmen (GPS coordinates 6291936, 418067, SWEREF99 TM) is raw water from 4.5 meters depth, collected 4th of March 2015 prior intake into Ringsjöverket DWTP. The organic carbon in water from lake Görväln is mainly autochthonous; i.e. produced by bacteria and algae within the lake, while the organic carbon in lake Bolmen mainly has terrestrial origin and thus is allochthonous.

The raw water was filtrated using glass fibre filters (Munktell Glass Microfibre Disc MG 160, 142 mm diameter, pore size ~1 μm) at a speed of 140 rpm, approximately 0.23 L min^{-1}, using a peristaltic pump (Masterflex® L/S®, easy-load 3, model 77800-62). Initial DOC concentrations were measured; Bolmen 10 mg L^{-1} and Görväln 8.3 mg L^{-1}, and the two water types were thereafter diluted with Millipore water into 10 L containers

to DOC concentrations 2, 4 and 8.3 mg L^{-1} respectively. Millipore water was used as DOC concentration 0 mg L^{-1}. Each container was spiked with 50 μL of a standard mix solution (BSX9) containing 14 PFASs with a concentration of 500 μg mL^{-1} per individual PFAS, resulting in a final concentration of 2.5 μg L^{-1} per individual PFAS in each container. The water containers were stored in a dark room at 5°C. Before the experiment, GAC was preconditioned in Millipore water for five days without stirring, stored at room temperature and covered with a cardboard box to minimize photosynthetic reactions. AE was rinsed three times prior experiment, using Millipore water.

Pretests were performed to determine the amount of GAC or AE to be used (Figure A4 in Appendix D). The pretests were performed using five different amounts of GAC to determine which amount would reduce the DOC concentration by 50%; a too high amount of GAC might reduce the DOC concentration to non-detectable levels, and a too small amount might lead to that no difference between initial and final sample is detected. Pretests were performed only on DOC, using 1.5, 2, 2.5, 3 and 6 g L^{-1} GAC and AE, respectively. PFAS analysis was not included in the pretests due to the time-consuming analysis of PFAS concentrations. The amount of GAC or AE used further in the experiments was set to 10 g L^{-1}.

A water volume of 800 mL was weighted into 1000 mL glass beakers. Sodium bicarbonate with a final concentration of 0.25 mM was added to each beaker as buffer solution. GAC or AE (8 g) was added to each beaker and directly afterwards the samples were stirred for 15 minutes at 250 rpm using a flocculator (Flocculator Nr: 210, KEMIRA) (Figure 4; Figure A6 in Appendix F). After stirring, the GAC or AE was allowed to settle for five minutes before sampling into two 50 mL PP-tubes. The samples were stored in a dark room at 5°C prior PFAS analysis. All samples were performed in duplicates and a pre sample of all waters was collected before addition of GAC or AE.

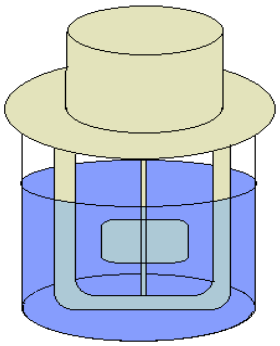

Figure 4. Illustration of glass beaker with flocculator stirring the water.

3.4 PFAS analysis

All glassware used was washed with tap water, rinsed with ethanol, washed in dish washer and burnt in the oven at 400°C. Before use, all glassware was rinsed with methanol.

Initially, samples from the column experiment were filtered using vacuum and glass fiber filters (Whatman™ Glass Microfiber Filters GF/C™, 47 mm diameter, 1.2 μm). Following filtration, solid phase extraction (SPE) (Figure A7 in Appendix G) was performed on both column and batch experiment samples to extract the PFASs, according to Ahrens et al. (2009a). The samples were spiked with 100 μL of an IS mixture (concentration 50 pg μL^{-1}). After the SPE equipment was assembled (using Oasis® WAX 6cc cartridges, 6 cm^3, 500 mg, 60 μm for column experiments and 150 mg, 30 μm for batch experiments, by Waters, Massachusetts USA), the SPE was preconditioned with 4 mL 0.1% ammonium hydroxide in methanol followed by 4 mL methanol and 4 mL Millipore water. The flow was regulated to one drop per second. If needed, vacuum was used. After extraction was completed, the cartridges were washed with 4 mL 25 mM

ammonium acetate buffer in Millipore water. The PFASs were eluted using 6 mL methanol followed by 6 mL 0.1% ammonium hydroxide in methanol, and the samples were concentrated to 1 mL using nitrogen evaporation (N-EVAP™ 112). The samples were analyzed using high performance liquid chromatography-mass spectrophotometry (HPLC-MS/MS) (Ahrens et al., 2009a).

3.5 Quality control and quality assurance

Since PFASs are present in our everyday environment, there is a potential risk for contamination during experiments and analyses. Therefore blanks were run during each SPE (n=2), making it possible to correct for potential contamination. During SPE, blanks and samples were spiked with IS, and extracted to determine the recovery efficiency of each PFAS. Positive controls, without addition of GAC or AE, were run in parallel during the batch experiments. This made it possible to correct for other possible removal mechanisms than adsorption to GAC and AE, such as adsorption to the equipment used or evaporation to the air. During the batch experiments, the samples were run in duplicates.

4 Results

4.1 Pilot scale column experiments at Bäcklösa DWTP

The average flow rate through the GAC column was 36.3±1.3 mL min^{-1}, while the flow rate through the AE column was 36.0±1.8 mL min^{-1}. During the experiment (140 days) 33 223 BVs (Equation 1) spiked water have been treated using GAC and 41 452 BVs have been treated using AE. The average EBCT (Equation 2) was 6.1 minutes for GAC and 4.9 minutes for AE. The removal efficiency was calculated as a percentage, using the PFAS concentration in the samples collected from the GAC or AE column compared to the concentration in the reservoir (Equation 3). Due to varying concentrations in the reservoir during the experimental period (Figure A1; Table A3 in Appendix B), the average concentration of each PFAS in the reservoir was used during the calculations. Due to analytical failure, the sixth time point (day 29) for GAC (7035 BVs) was not included in the results. The analyzed standard water parameters did not change over the experimental period. However, the DOC concentration in the collected samples changed before and after GAC and AE treatment (Table A2 in Appendix A).

4.1.1 Granular activated carbon

Ten PFCAs were detected in the samples (Figure 5a,b). The removal efficiency of long-chained PFCAs (C_8-C_{11}, C_{13}) was >55% during the 140 day (33 223 BVs) experimental period (Figure 5b), while the short-chained PFCAs (C_3-C_7) were less efficiently removed, ranging between 24% and 46% (C_4-C_7) (Figure 5a), compared to the longer-chained PFCAs. The general trend of the PFCAs was a decrease in removal efficiency with increasing number of BVs. However, PFPeA displayed a different behavior; the removal efficiency of PFPeA dropped between 10 813 and 21 576 BVs, ranging between -29% and -68% during that period. In addition, the removal efficiency of PFBA decreased to negative values after 23 240 BVs (Figure 5a). Among the short-chained PFCAs (C_3-C_7; Figure 5a), PFOA (C_7) had the highest average removal efficiency after 33 223 BVs (71±18%) and thereafter average removal efficiency decreased with decreasing perfluorocarbon chain length (Table 2). Among the long-chained PFCAs (C_8-C_{11}, C_{13}; Figure 5b), average removal efficiency increased with increasing perfluorocarbon chain length (Table 2).

Table 2. Average removal efficiency (%) after 33 223 BVs and removal efficiency after final sampling (%) (day 140, 33 223 BVs) for the investigated PFASs for the GAC column experiments

PFAS	Average (*n*=21) (%)	After final sampling at 33 223 BVs (%)
PFBA (C_3)	21±32	-12
PFPeA (C_4)	14±52	24
PFHxA(C_5)	54±24	23
PFHpA (C_6)	62±22	32
PFOA(C_7)	71±18	46
PFNA (C_8)	77±15	57
PFDA (C_9)	80±13	62
PFUnDA (C_{10})	82±11	67
PFDoDA (C_{11})	81±11	73
PFTeDA (C_{13})	82±11	80
FOSA (C_8)	85±10	69
PFBS (C_4)	53±27	39
PFHxS (C_6)	75±16	57
PFOS (C_8)	86±10	72

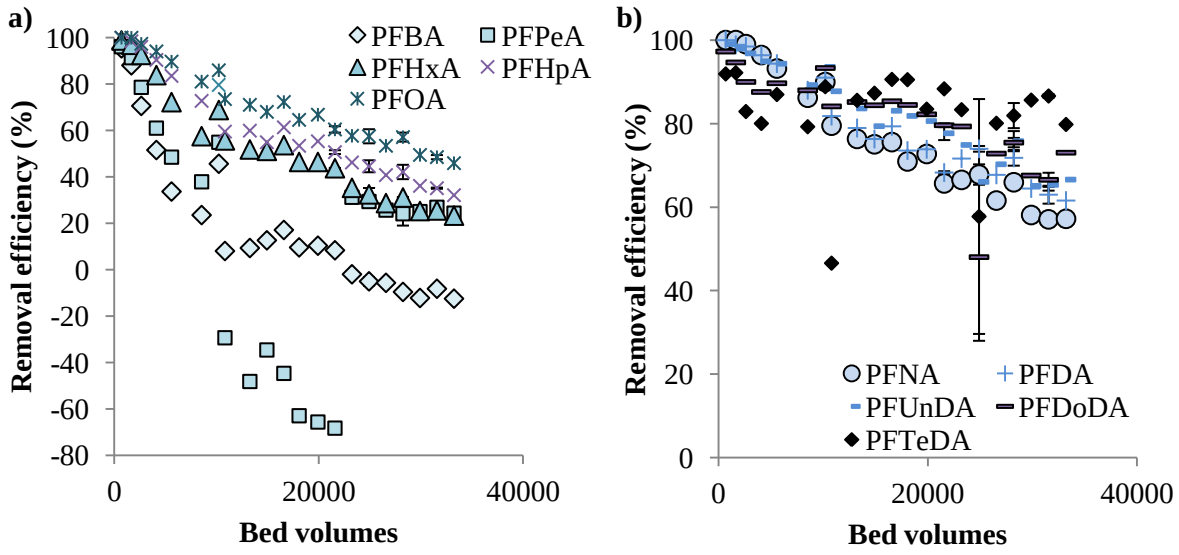

Figure 5. Removal efficiency of a) short-chained PFCAs (C_3-C_7) and b) long-chained PFCAs (C_8-C_{11}, C_{13}) in the GAC column. Duplicate samples from the columns were collected and analyzed after 91, 105, 119 and 133 days, standard deviation presented as error bars.

FOSA was detected in all samples (Figure 6a). The removal efficiency decreased over the 140 days during which the experiment was performed, with an average removal efficiency of 85±10%. The removal efficiency of FOSA after 140 days (33 223 BVs) was 69%. In addition, all spiked PFSAs were detected in the samples collected (Figure 6b). The removal efficiency of PFHxS and PFOS decreased as the number of BVs increased. The average removal efficiency of PFHxS and PFOS was 75±16% and 86±10%, respectively, and the removal efficiency after 140 days (33 223 BVs) was 57% and 72%, respectively. PFBS has the shortest fluorocarbon chain length among the detected PFSAs (C_4) and, in addition, displayed the most rapid decrease in removal efficiency (Figure 6b). Average removal efficiency of PFBS was 53±27% and the removal efficiency after 140 days (33 223 BVs) was 39%.

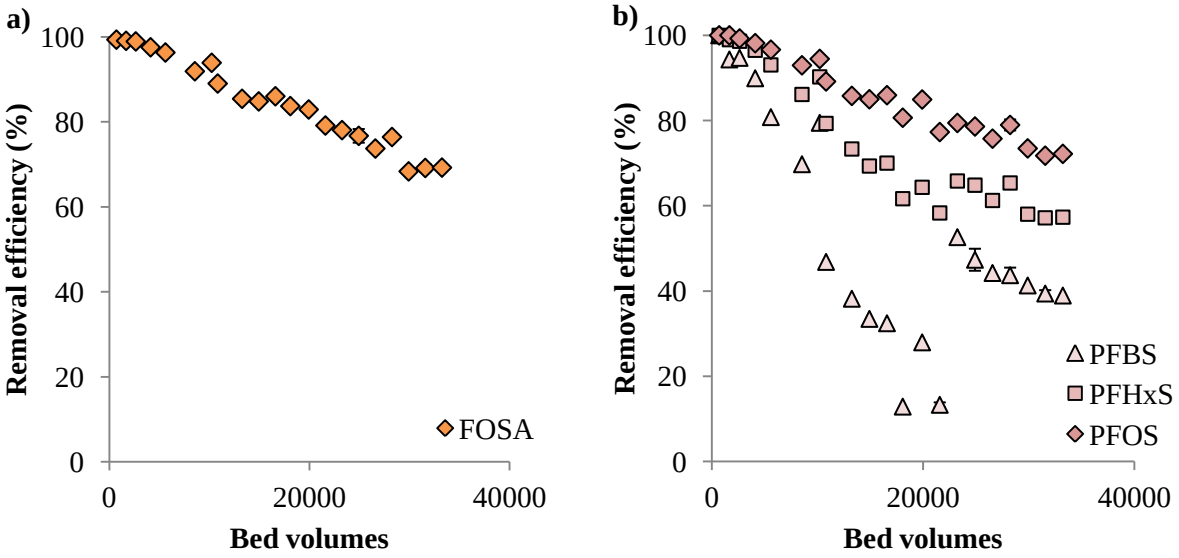

Figure 6. Removal efficiency of a) FOSA and b) PFSAs in the GAC column. Duplicate samples from the columns were collected and analyzed after 91, 105, 119 and 133 days, standard deviation presented as error bars.

The adsorption of individual PFASs (μg g^{-1} GAC) generally increased linearly over the 140 day experimental period (Figure 7a,b,c,d). However, PFPeA and PFBA displayed a different behavior, as PFPeA started to decrease after 10 813 BVs and thereafter increase once more after 21 576 BVs, while PFBA on the other hand levelled off after approximately 10 000 BVs and decreased slowly after 21 576 BVs (Figure 7a). A total of 43 μg $\sum$PFASs g^{-1} GAC was adsorbed during the 140 day experimental period (Figure A2; Table A4 in Appendix C).

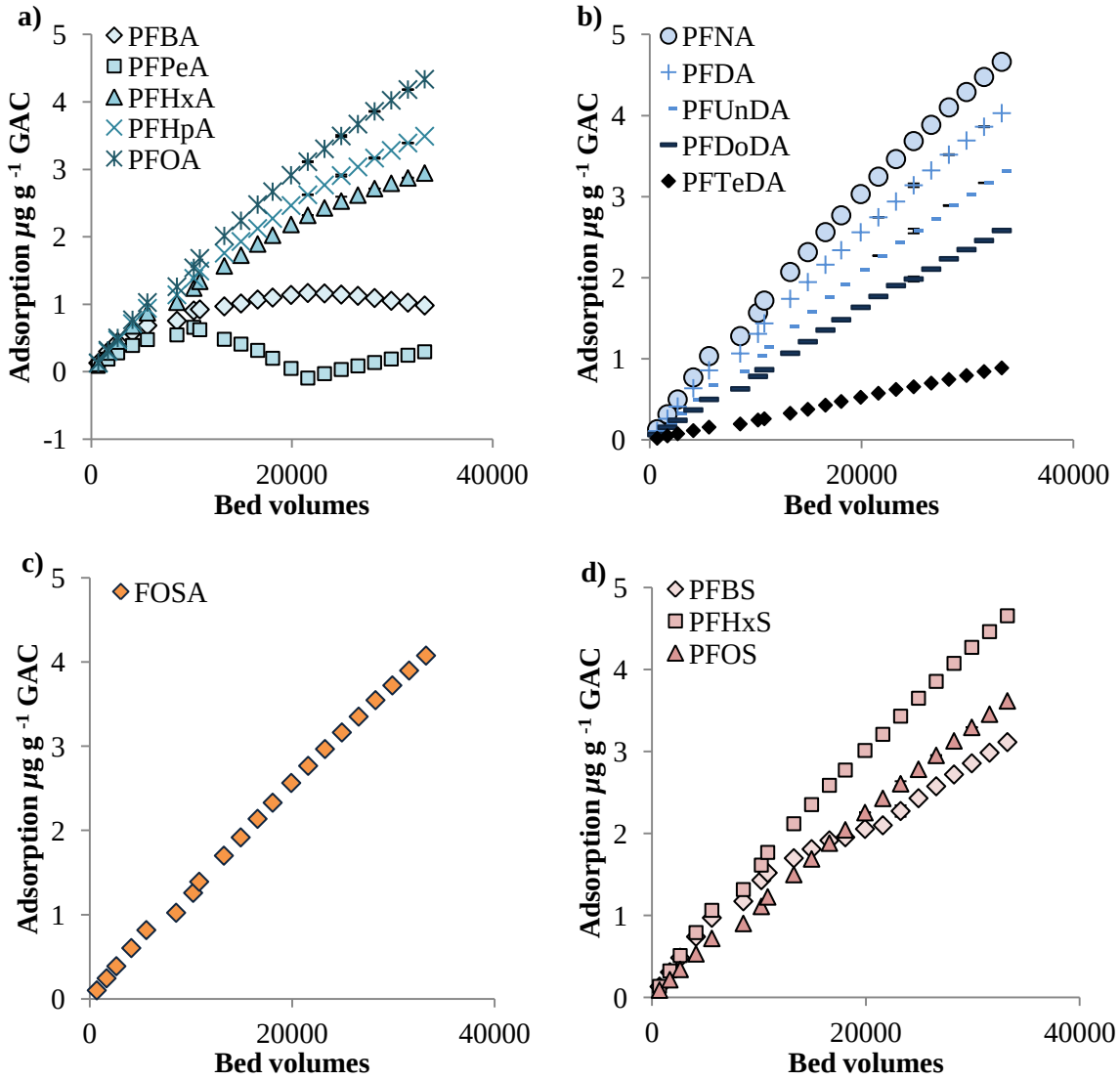

Figure 7. The cumulative adsorption of the investigated PFASs to GAC in μg g^{-1} GAC for a) short-chained PFCAs (C_3-C_7), b) long-chained PFCAs (C_8-C_{11}, C_{13}), c) FOSA and d) PFSAs. Duplicate samples from the columns were collected and analyzed after 91, 105, 119 and 133 days, standard deviation presented as error bars.

The removal efficiencies of PFCAs, PFSAs and FOSA based on perfluorocarbon chain length after day 3, 42, 98 and 140 are shown in figure 8a,b,c,d. The removal efficiency of PFCAs and PFSAs increased with perfluorocarbon chain length after 42, 98 and 140 days (Figure 8b,c,d). However, the result from the first sample (day 3, 693 BVs) indicated high removal efficiency of all investigated PFASs (ranging between 95% and 100%), regardless of the chain length (Figure 8a). After the final sampling (Figure 8d), day 140 (33 223 BVs), the removal efficiency for PFCAs ranged from -12% (C_3, PFBA) to 80%

(C_{13}, PFTeDA). For PFSAs the removal efficiency ranged from 39% (C_4, PFBS) to 72% (C_8, PFOS). The removal efficiency of PFSAs was higher comparing to PFCAs (Figure 8d). For the chain length C_4, PFBS had higher removal efficiency than PFPeA (39% and 24%, respectively); for C_6, PFHxS had higher removal efficiency than PFHpA (57% and 32%, respectively) and for C_8, PFOS had higher removal efficiency than PFNA (72% and 57%, respectively).

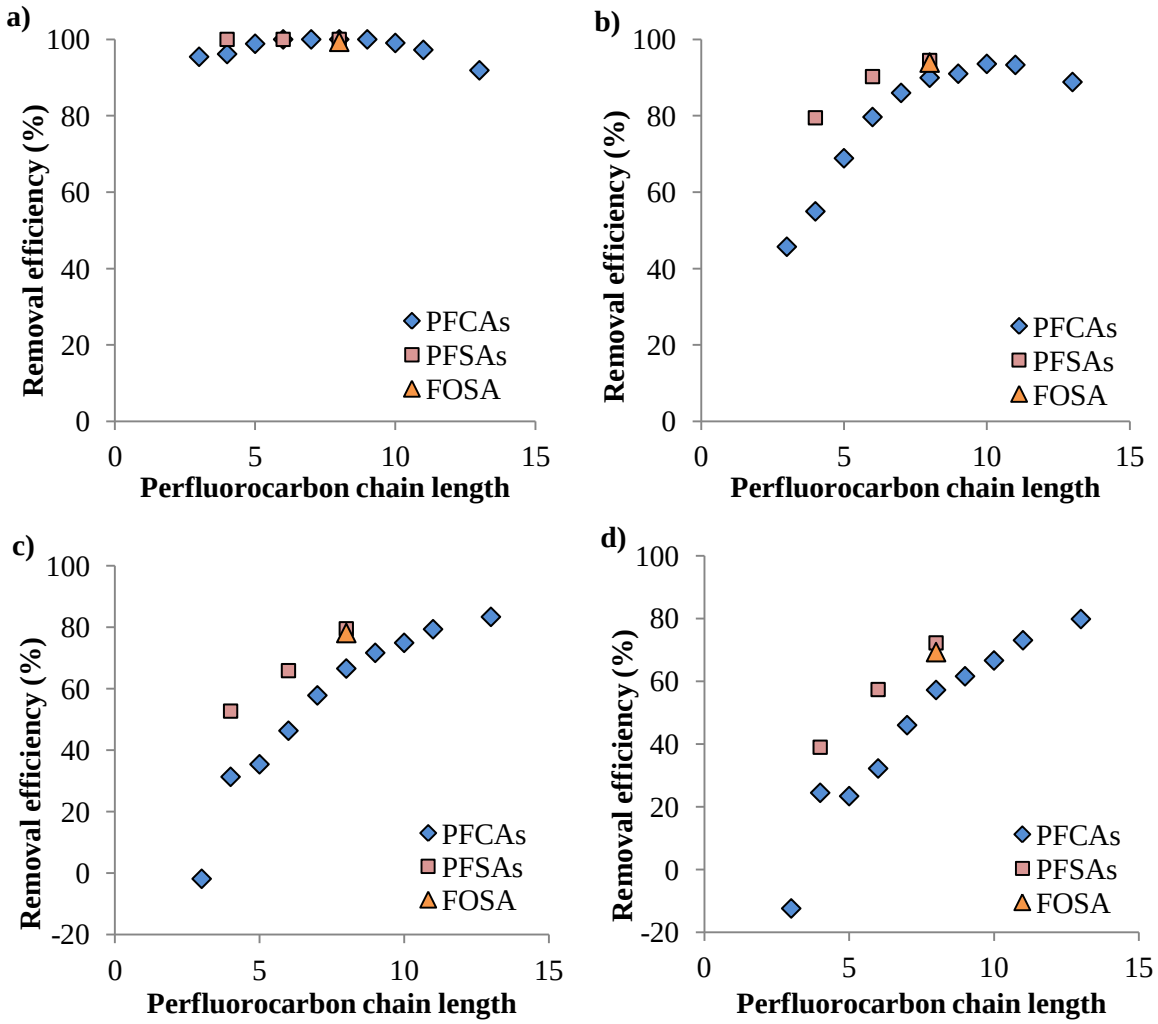

Figure 8. Removal efficiency against the perfluorocarbon chain length of PFCAs, PFSAs and FOSA, using GAC as adsorbent. Values are plotted from a) day 3, 693 BVs, b) day 42, 10 214 BVs, c) day 98, 23 240 BVs and d) day 140, 33 223 BVs.

4.1.2 Anion exchange

During the AE experiment, the same PFCAs as for the GAC experiment were detected (Figure 9a,b). In general, the trend was also similar, with decreasing removal efficiency as the number of BVs increased. Similar to the GAC treatment there was a major decrease in removal efficiency for PFPeA, leading to negative values (ranging between -13% and -180%) between 13 593 and 26 920 BVs. Additionally, there was also an increase in PFBA and PFHxA removal efficiency during the same interval. Among the short chained PFCAs (C_3-C_7, figure 9a), PFOA (C_7) had the highest average removal efficiency (72±20%) and thereafter the average removal efficiency generally decreased with perfluorocarbon chain length (Table 3). Among the long-chained PFCAs (C_8-C_{11}, C_{13}) the removal efficiency slowly decreased over 140 days (Figure 9b). Generally, the average removal efficiency increased with increasing chain-length (Table 3).

Table 3. Average removal efficiency (%) after 41 452 BVs and removal efficiency after final sampling (%) (day 140, 41 452 BVs) for the investigated PFASs for the AE column experiment

PFAS	Average (*n*=22) (%)	After final sampling at 41 452 BVs (%)
PFBA (C_3)	10±25	-14
PFPeA (C_4)	25±88	14
PFHxA(C_5)	31±38	-9.5
PFHpA (C_6)	54±30	8.0
PFOA(C_7)	72±20	39
PFNA (C_8)	83±13	63
PFDA (C_9)	88±8.4	77
PFUnDA (C_{10})	92±5.0	84
PFDoDA (C_{11})	89±4.7	88
PFTeDA (C_{13})	81±12	79
FOSA (C_8)	89±7.9	74
PFBS (C_4)	70±25	60
PFHxS (C_6)	90±12	86
PFOS (C_8)	96±6.3	96

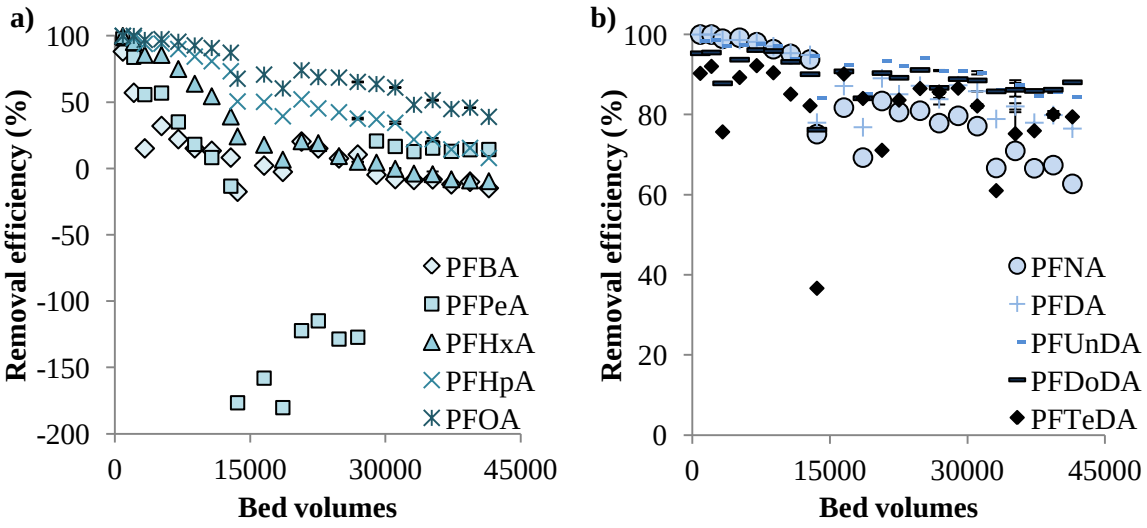

Figure 9. Removal efficiency of a) short-chained PFCAs (C_3-C_7) and b) long-chained PFSAs (C_8-C_{11}, C_{13}) in the AE column. Duplicate samples from the columns were collected and analyzed after 91, 105, 119 and 133 days, standard deviation presented as error bars.

FOSA was present in all samples with a removal efficiency was 89±7.9%.The removal efficiency of FOSA decreased during the entire 140 day experimental period, with a removal efficiency after last sampling (41 452 BVs) of 74% (Figure 10a). Among the PFSAs, both PFHxS and PFOS were efficiently removed (average removal efficiency 90±12% for PFHxS and 96±6.3% for PFOS) during the 140 day period, with sudden drops in removal efficiency after 13 593, 18 610 and 33 148 BVs (Figure 10b). The removal efficiency of PFHxS and PFOS after 140 days (41 452 BVs) was 86% and 96%, respectively. The removal efficiency of PFBS varied between 13% and 100% during the experiment, with an average removal efficiency of 70±25% and a removal efficiency of 60% after 140 days (41 452 BVs).

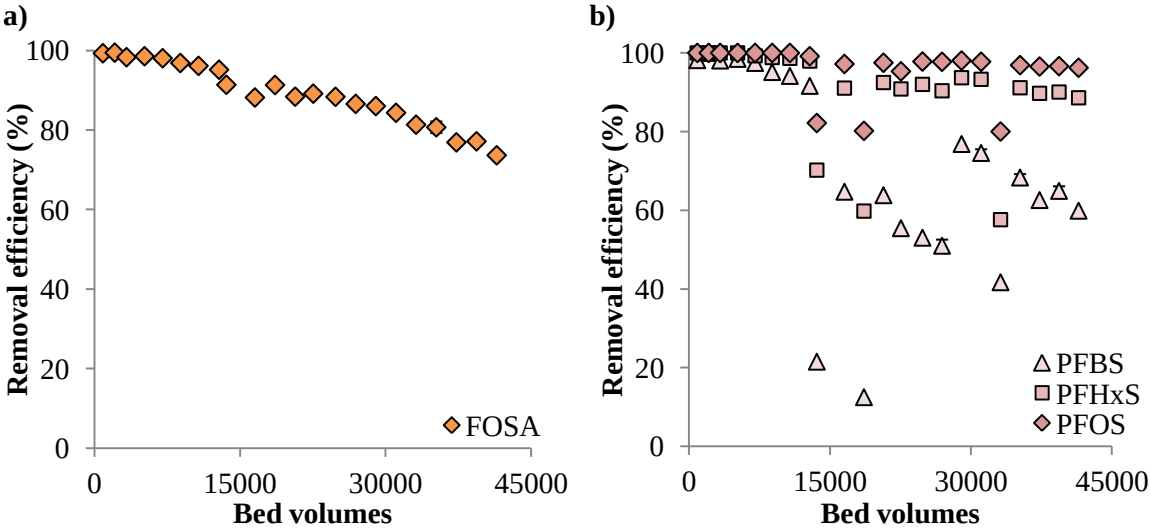

Figure 10. Removal efficiency of a) FOSA and b) PFSAs in the AE column. Duplicate samples from the columns were collected and analyzed after 91, 105, 119 and 133 days, standard deviation presented as error bars.

In general, the adsorption of individual PFASs (μg g^{-1} AE) increased linearly with increasing number of BVs (Figure 11a,b,c,d). There were however exceptions; PFBA levelled off after approximately 5 000 BVs and started to decrease slightly after 26 920 BVs. In addition, PFPeA also levelled off and started to decrease after 12 840 BVs, reaching a negative value for adsorption. The total concentration of all PFASs adsorbed after 140 days was approximately 45μg g^{-1} AE resin (Figure A3; Table A5 in Appendix C).

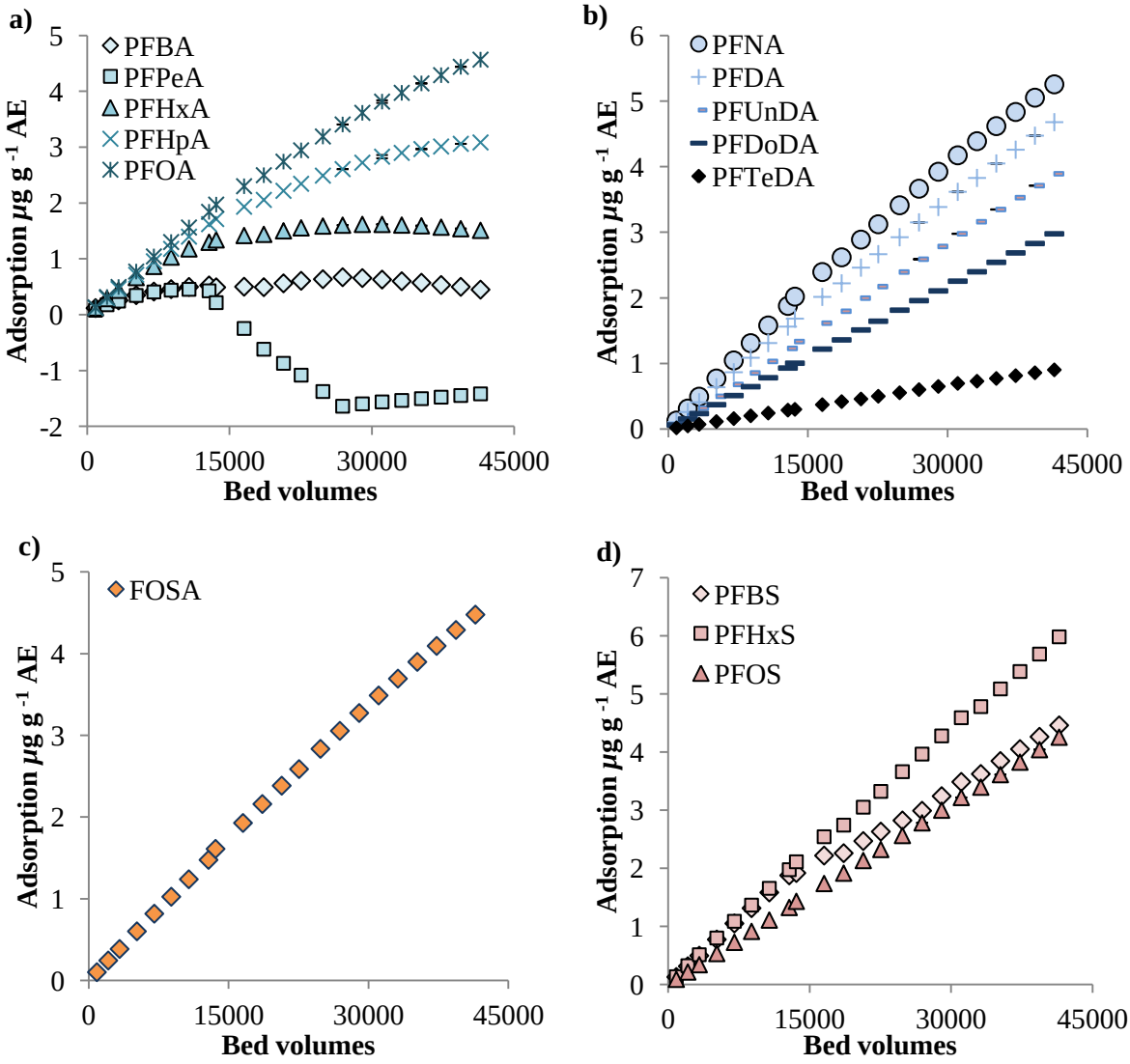

Figure 11. The cumulative adsorption in μg g^{-1} AE for a) short-chained PFCAs (C_3-C_7), b) long-chained PFCAs (C_8-C_{11}, C_{13}), c) FOSA and d) PFSAs. Duplicate samples from the columns were collected and analyzed after 91, 105, 119 and 133 days, standard deviation presented as error bars.

The removal efficiencies of PFCAs, PFSAs and FOSA based on perfluorocarbon chain length after day 3, 42, 98 and 140 are shown in figure 12a,b,c,d. The removal efficiency of PFCAs and PFSAs generally increased with perfluorocarbon chain length after 42, 98 and 140 days (Figure 12b,c,d). However, the result from the first sample (day 3, 871 BVs) indicated high removal efficiency of the investigated PFASs (ranging between 88% and 100%), regardless of chain length (Figure 12a). After the final sampling (Figure 12d), day 140 (33 223 BVs), the removal efficiency of PFCAs varied between -15% (C_3, PFBA) and 88% (C_{11}, PFDoDA). The removal efficiency of PFSAs on the other hand, ranged between 60% (C_4, PFBS) and 96% (C_8, PFOS). PFSAs were more efficiently removed compared to PFCAs. For C_4, PFBS had higher removal efficiency than PFPeA (60% and 14%, respectively). When comparing the C_6 chain length, PFHxS had higher removal efficiency than PFHpA (89% and 8.0%, respectively), and for C_8, PFOS had higher removal efficiency than PFNA (96% and 63%, respectively).

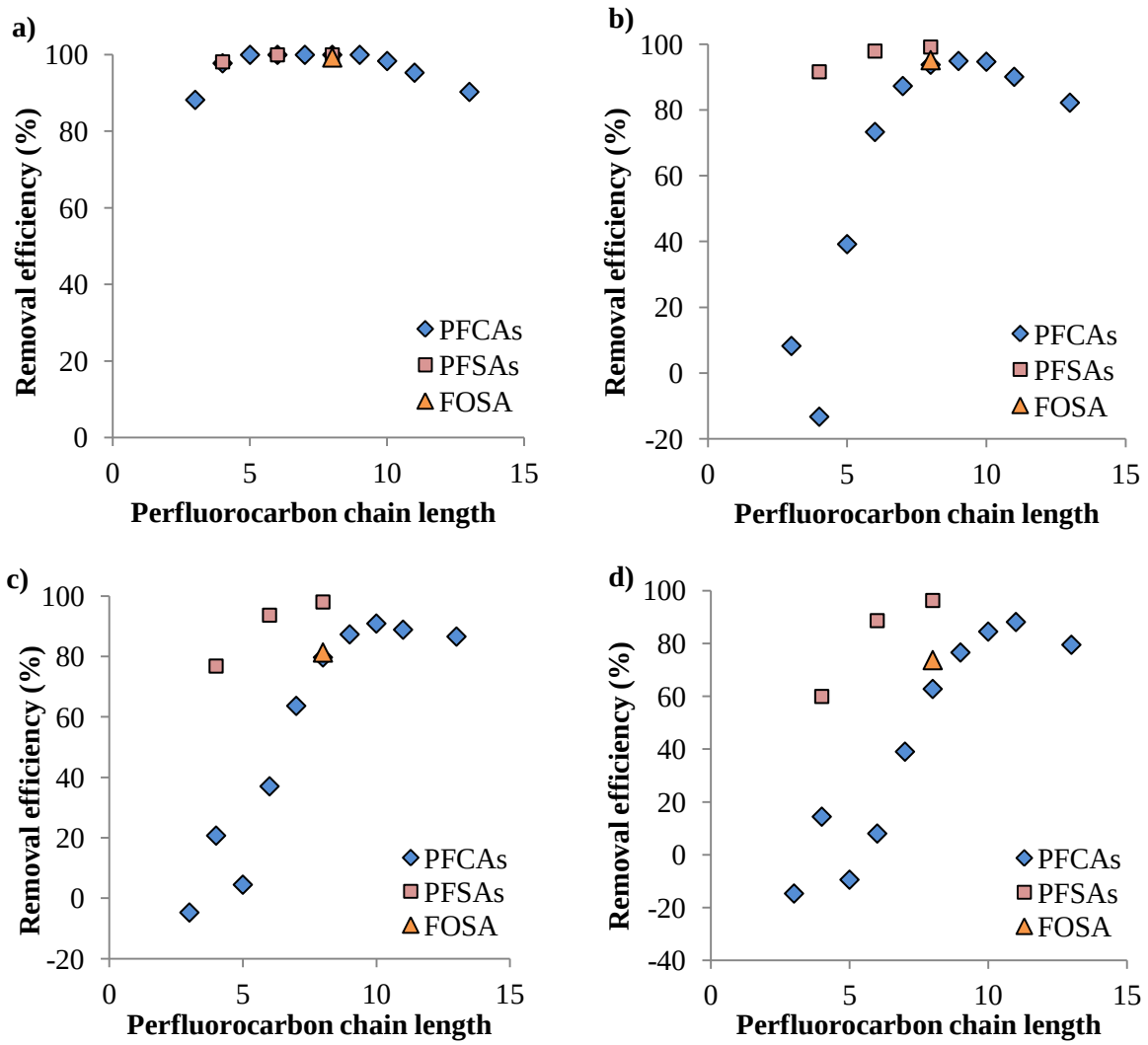

Figure 12. Removal efficiency against the perfluorocarbon chain length of PFCAs, PFSAs and FOSA, using AE as adsorbent. Values are plotted from a) day 3, 871 BVs, b) day 42, 12 840 BVs, c) day 98, 28 996 BVs and d) day 140, 41 452 BVs.

4.1.3 Comparison removal efficiency of linear and branched PFASs

The perfluorocarbon chain of PFASs can either be linear or branched, resulting in differences in environmental behavior between the isomers (Rahman et al., 2014). A comparison between removal efficiency of linear and branched PFOS indicated that AE was equally efficient in adsorbing both linear and branched PFOS (removal efficiency after 41 452 BVs was 96% and 96%, respectively) (Figure 13a). In contrast, GAC adsorbed linear PFOS more efficiently than branched, with a removal efficiency after 33 223 BVs of 86% and 78%, respectively (Figure 13b).

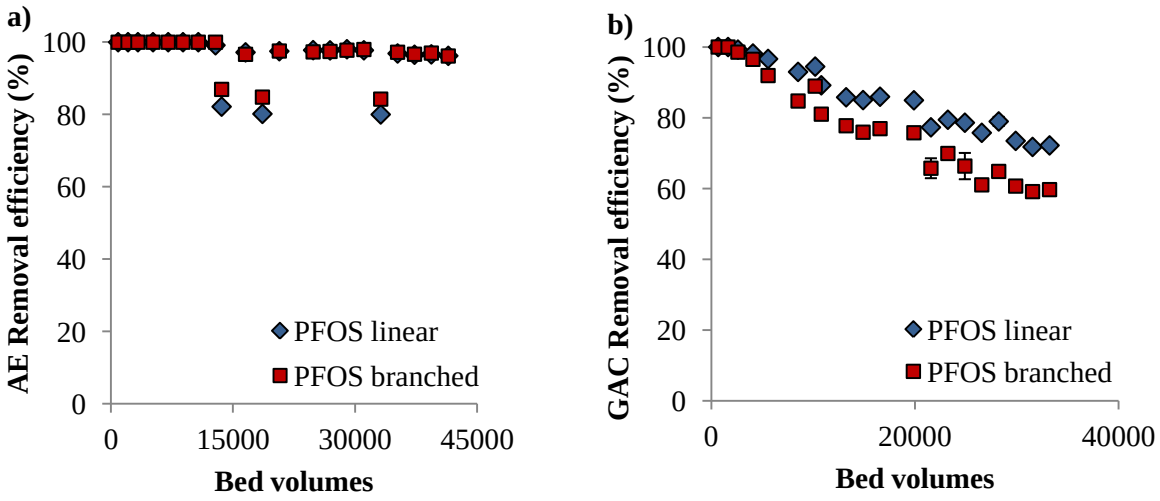

Figure 13. Removal efficiency of linear and branched PFOS using a) AE and b) GAC. Duplicate samples from the columns were collected and analyzed after 91, 105, 119 and 133 days, standard deviation presented as error bars.

Similarly to PFOS, both linear and branched FOSA and PFHxS were equally removed by AE (Figure 14a; Figure 15a). However, branched FOSA and PFHxS were less efficiently removed by GAC compared to their linear isomers (Figure 14b; Figure 15b). Removal efficiency of linear and branched FOSA after 41 452 BVs using AE was 74% and 73%, respectively, while removal efficiency after 33 223 BVs using GAC was 69% for linear and 57% for branched. For PFHxS the removal efficiency after 41 452 BVs using AE was 89% for linear and 88% for branched, while removal efficiency after 33 223 BVs using GAC was 57% for linear and 40% for branched.

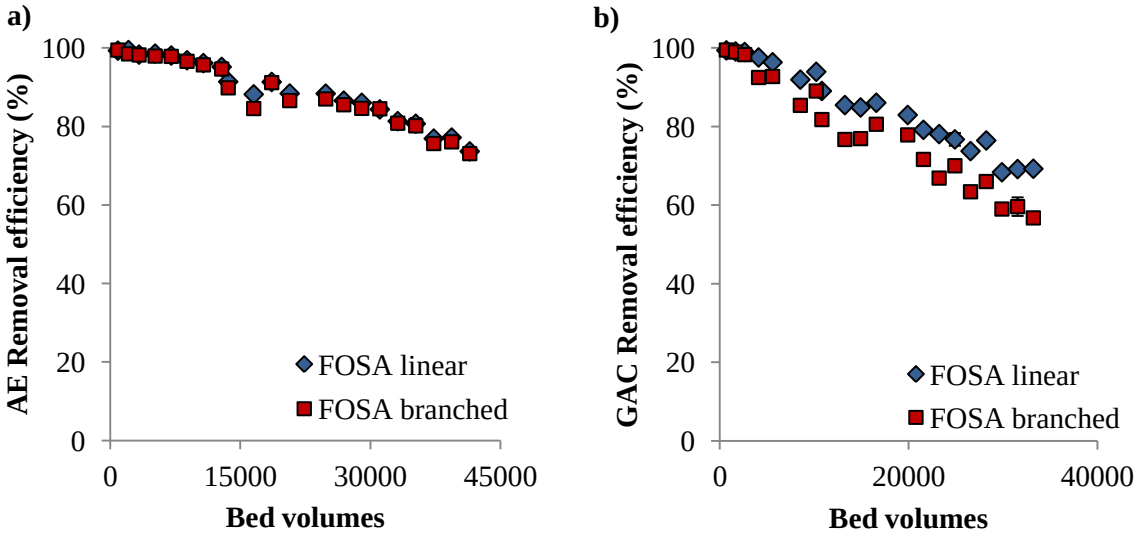

Figure 14. Removal efficiency of linear and branched FOSA using a) AE and b) GAC. Duplicate samples from the columns were collected and analyzed after 91, 105, 119 and 133 days, standard deviation presented as error bars.

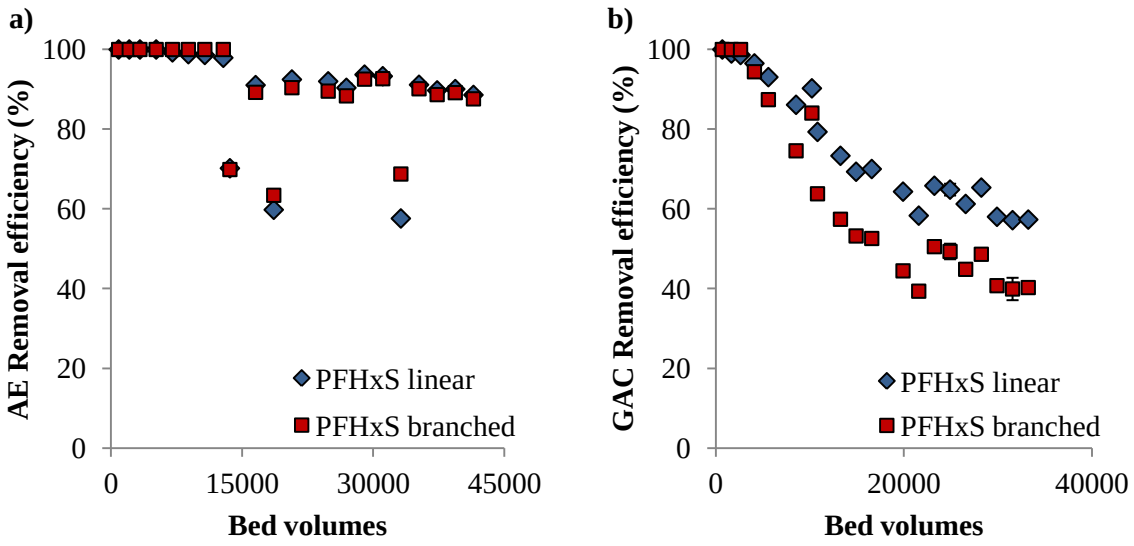

Figure 15. Removal efficiency of linear and branched PFHxS using c) AE and d) GAC. Duplicate samples from the columns were collected and analyzed after 91, 105, 119 and 133 days, standard deviation presented as error bars.

4.2 Laboratory batch experiments

During the experiment, two different water types with DOC concentrations 0, 2, 4 and 8.3 mg L^{-1} were spiked with 14 PFASs. The fraction of PFASs not adsorbed to GAC or AE was calculated as concentration at the end of the experiment compared to initial concentration in the water (C/C_0), i.e. lower C/C_0 values correspond to higher sorption to the respective adsorbent (GAC or AE).

4.2.1 Granular activated carbon

A comparison between C/C_0 for the 14 investigated PFASs and the influence of DOC concentration using diluted water from lake Görväln is displayed in figure 16. The PFCA adsorption to GAC generally increased as DOC was present in the water, and the increase was larger at DOC concentrations 4 and 8.3 mg L^{-1} compared to 2 mg L^{-1}. However, the adsorption of PFBA (C_3) slightly decreased in the presence of DOC (C/C_0 from 0.18±0.02 in the absence of DOC to 0.25±0.02 in the presence of DOC). For the longer-chained PFCAs PFUnDA (C_{10}) and PFDoDA (C_{11}), DOC concentration 2 mg L^{-1} resulted in similar adsorption as when DOC was absent, while DOC concentrations 4 and 8.3 mg L^{-1} led to increased adsorption. In addition, the adsorption of PFTeDA (C_{13}) varied greatly comparing C/C_0 with the different DOC concentrations. FOSA displayed increased adsorption as DOC concentration increased. For the short-chained PFSA PFBS (C_4) adsorption increased as DOC was present, although DOC concentrations 4 and 8 mg L^{-1} resulted in similar adsorption efficiency. For the longer-chained PFSAs PFHxS (C_6) and PFOS (C_8), the adsorption increased as the DOC concentration increased. However, for PFHxS (C_6), the adsorption decreased at DOC concentration 2 mg L^{-1}.

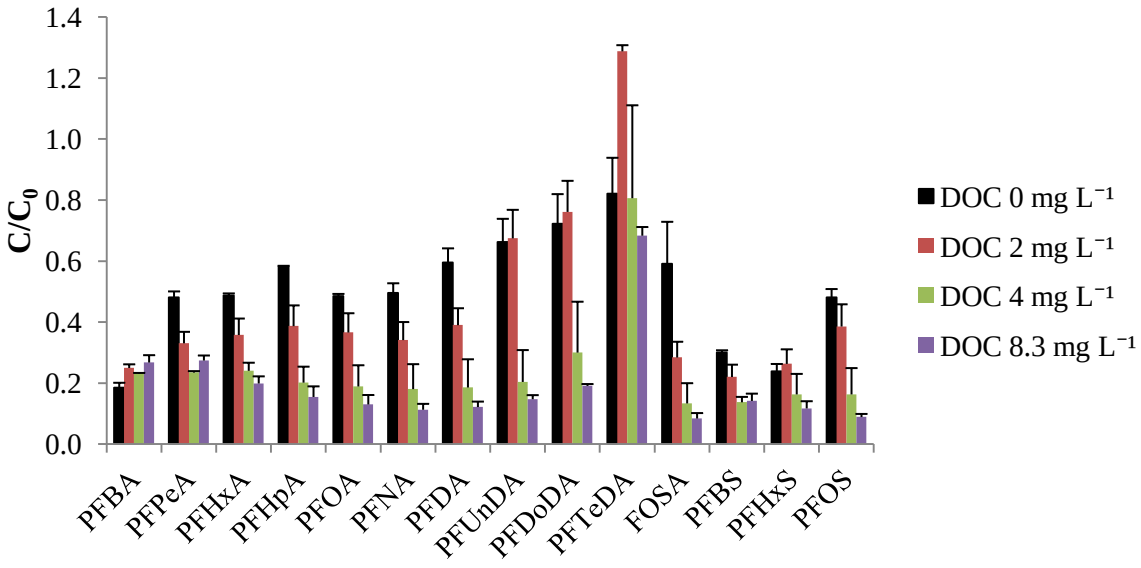

Figure 16. Concentration at the end of the experiment compared to initial concentration (C/C_0) using GAC as adsorbent, and the influence of DOC, for the 14 investigated PFASs. Experiments performed in duplicate, standard deviation presented as error bars, using water from lake Görväln.

The adsorption of PFASs to GAC in diluted water from lake Görväln depended on concentration of DOC present and perfluorocarbon chain length (Figure 17). The adsorption was highest in water with the highest DOC concentrations (4 and 8.3 mg L^{-1}) and decreased with decreasing DOC concentration. For example, average C/C_0 for PFNA, FOSA and PFOS (all C_8) was 0.10±0.02 for DOC 8.3 mg L^{-1}, 0.16±0.06 for DOC 4 mg L^{-1}, 0.34±0.07 for DOC 2 mg L^{-1} and 0.52±0.08 for DOC 0 mg L^{-1}. In addition, adsorption decreased with increasing perfluorocarbon chain length as the chain length increased over eight carbons.

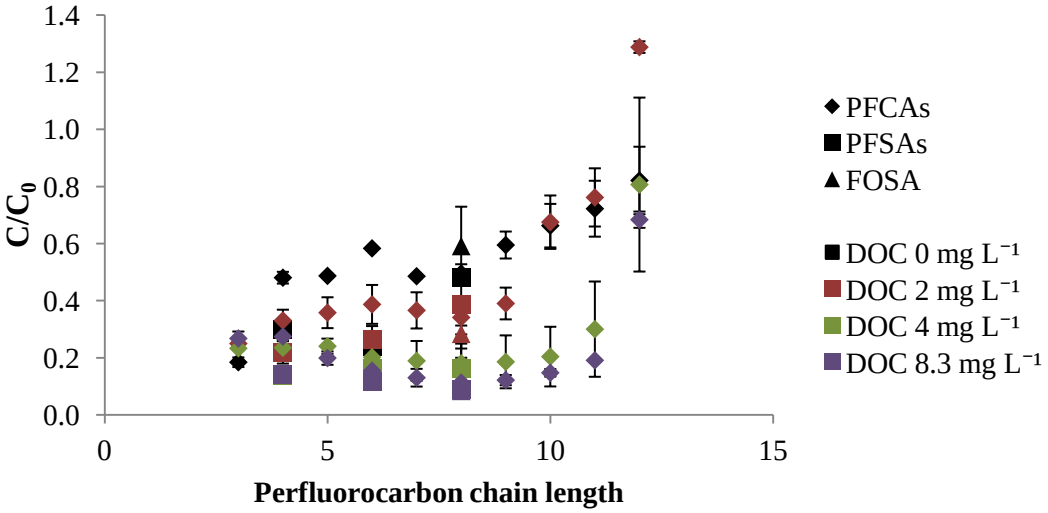

Figure 17. Correlation between perfluorocarbon chain length and C/C_0 (concentration at the end of the experiment compared to initial concentration) and the influence of DOC concentration, using water from lake Görväln and GAC as adsorbent. Experiments performed in duplicate, standard deviation presented as error bars. The shape of the symbol illustrates the compound or subclass and color illustrate DOC concentration.

Figure 18 illustrates the correlation between C/C_0 and DOC concentration for the 14 investigated PFASs when water from lake Bolmen was used. Similarly to when using water from lake Görväln, the adsorption of shorter-chained PFCAs (C_4-C_7) increased when DOC was present; all DOC concentrations led to similar increase in adsorption. For PFNA (C_8) and PFDA (C_9), the higher DOC concentrations (4 and 8.3 mg L^{-1}) resulted in higher adsorption. For the longer-chained PFASs (C_{10}-C_{11} and C_{13}), there was no correlation between adsorption and DOC concentration. In addition, the adsorption of PFBA (C_3) decreased as DOC concentration increased. For FOSA, the adsorption increased with DOC present; all DOC concentrations resulted in similar adsorption. The general trend for PFSAs was increased adsorption in water with DOC concentrations 4 and 8.3 mg L^{-1}. However, for PFHxS (C_6), the adsorption decreased as DOC was present.

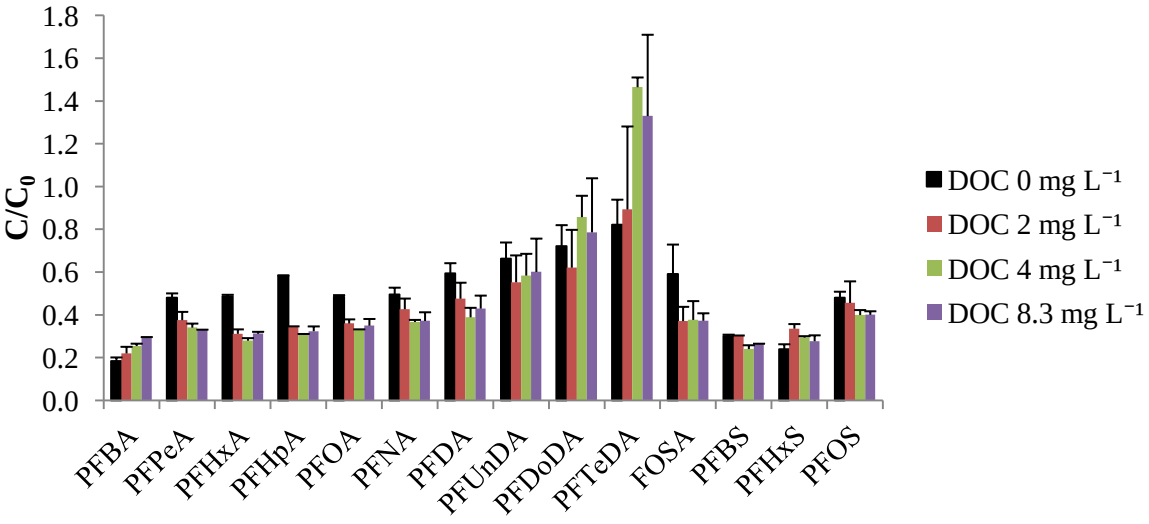

Figure 18. Concentration at the end of the experiment compared to initial concentration (C/C_0) using GAC as adsorbent, and the influence of DOC, for the 14 investigated PFASs. Experiments performed in duplicate, standard deviation presented as error bars, using water from lake Bolmen.

For all investigated DOC concentrations using water from lake Bolmen, adsorption of the investigated PFASs decreased as the perfluorocarbon chain length increased (Figure 19). PFCAs with chain lengths $<C_8$ displayed higher adsorption to GAC when DOC was present compared to samples were DOC was absent.

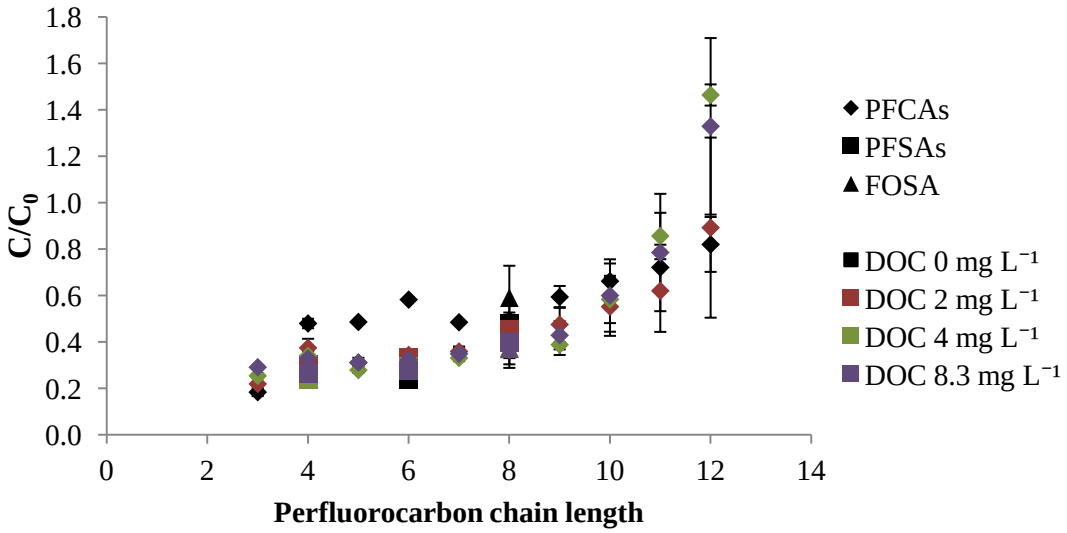

Figure 19. Correlation between perfluorocarbon chain length and C/C_0 (concentration at the end of the experiment compared to initial concentration) and the influence of DOC concentration, using water from lake Bolmen and GAC as adsorbent. Experiments performed in duplicate, standard deviation presented as error bars. The shape of the symbol illustrates the compound or subclass and color illustrate DOC concentration.

4.2.2 Anion exchange

A comparison between C/C_0 and DOC concentration for the 14 PFASs is shown in figure 20. During this experiment, water from lake Görväln was used. The general trend for PFCAs, FOSA and PFSAs was decreased adsorption as DOC was present and, in general, all DOC concentrations decreased the adsorption equally. However, PFTeDA (C_{13}) displayed varying results in C/C_0 comparing the different DOC concentrations. As the chain length of the PFCAs and PFSAs increased, the difference between C/C_0 for DOC 0 mg L^{-1} and C/C_0 for DOC containing water generally increased, indicating decreasing adsorption in DOC containing water as chain length increased.

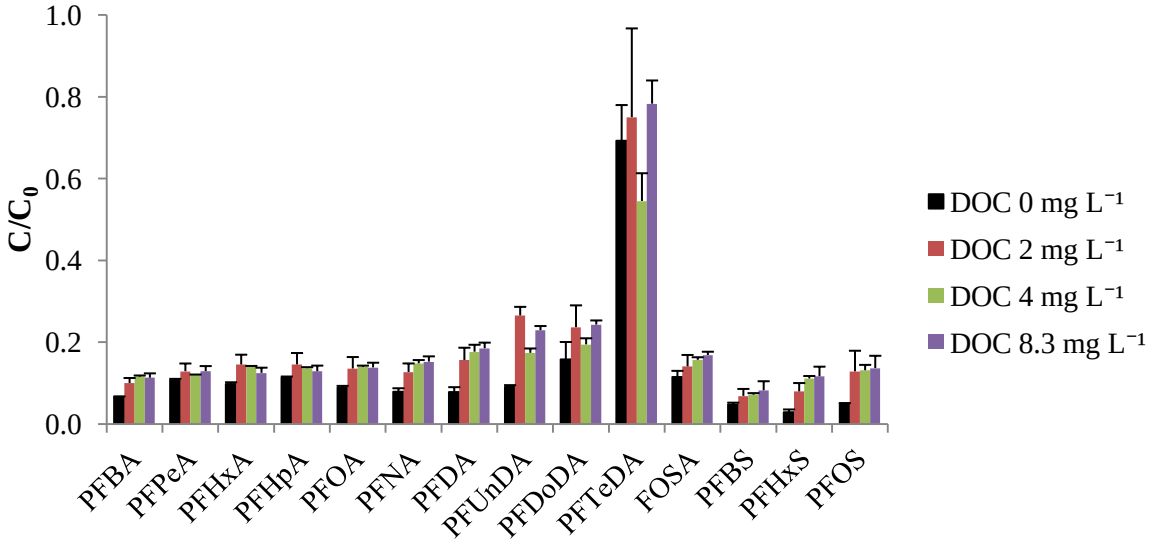

Figure 20. Concentration at the end of the experiment compared to initial concentration (C/C_0) using AE as adsorbent, and the influence of DOC for the 14 investigated PFASs. Experiments performed in duplicate, standard deviation presented as error bars, using water from lake Görväln.

During the experiments with AE using water from lake Görväln, adsorption of PFASs gradually decreased as the chain length increased over eight carbons (Figure 21). In addition, increased adsorption to AE was observed in absence of DOC.

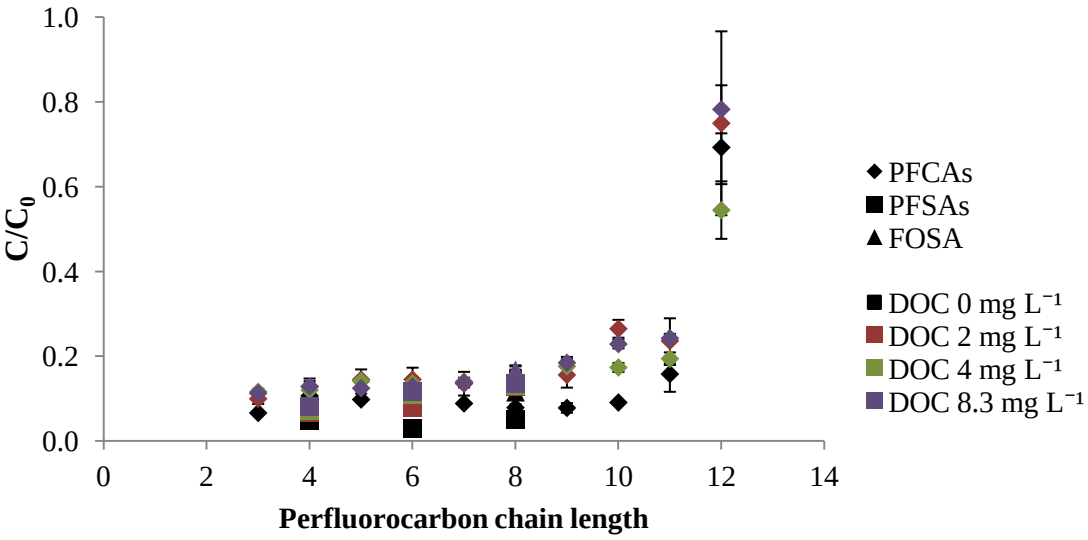

Figure 21. Correlation between perfluorocarbon chain length and C/C_0 (concentration at the end of the experiment compared to initial concentration) and the influence of DOC concentration, using water from lake Görväln and AE as adsorbent. Experiments performed in duplicate, standard deviation presented as error bars. The shape of the symbol illustrates the compound or subclass and color illustrate DOC concentration.

Similarly to when using water from lake Görväln to determine the correlation between C/C_0 and DOC concentration, experiments performed using water from lake Bolmen indicated decreased adsorption of PFCAs, FOSA and PFSAs when DOC was present (Figure 22). For short-chained PFCAs (C_3-C_7), PFUnDA (C_{10}) and PFDoDA (C_{11}) DOC concentration 4 mg L^{-1} caused the largest decrease in adsorption, while the largest decrease in adsorption of PFNA (C_8) and PFDA (C_9) resulted from DOC concentrations 4 and 8.3 mg L^{-1}, and 8.3 mg L^{-1}, respectively. PFTeDA (C_{13}) displayed varying results when comparing C/C_0 with the four different DOC concentrations. For FOSA and PFSAs presence of DOC decreased the adsorption, with DOC concentration 4 mg L^{-1} resulting in the highest decrease.

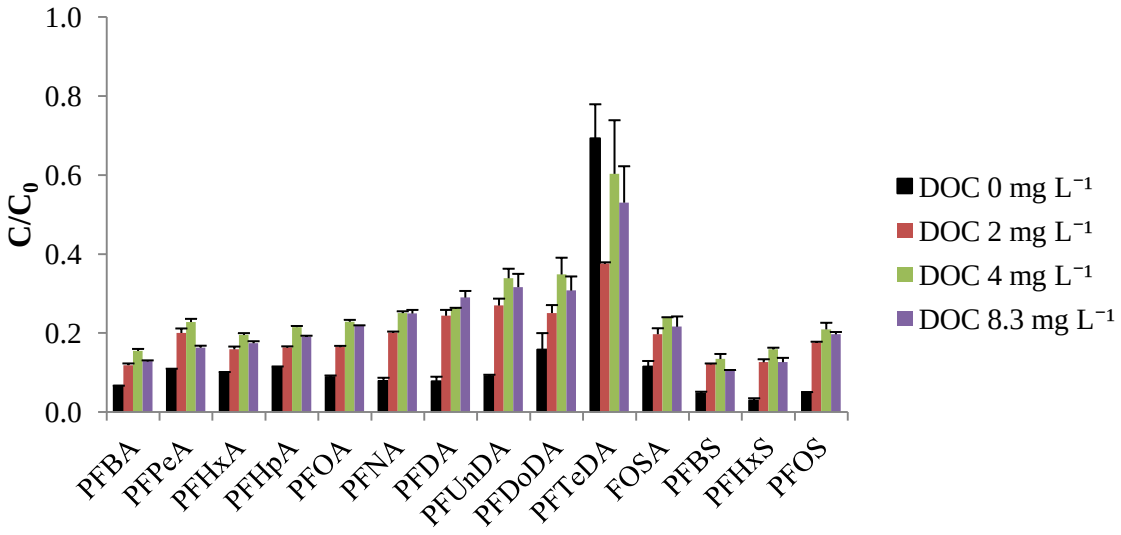

Figure 22. Concentration at the end of the experiment compared to initial concentration (C/C_0) using AE as adsorbent, and the influence of DOC for the 14 investigated PFASs. Experiments performed in duplicate, standard deviation presented as error bars, using water from lake Bolmen.

A comparison between C/C_0 and perfluorocarbon chain length indicated decreasing adsorption of the investigated PFASs as the chain length increased, using water from lake Bolmen (Figure 23). In addition, adsorption was affected by the DOC concentration in the water; as DOC was present, the adsorption to AE decreased, compared to C/C_0 in water where DOC was absent.

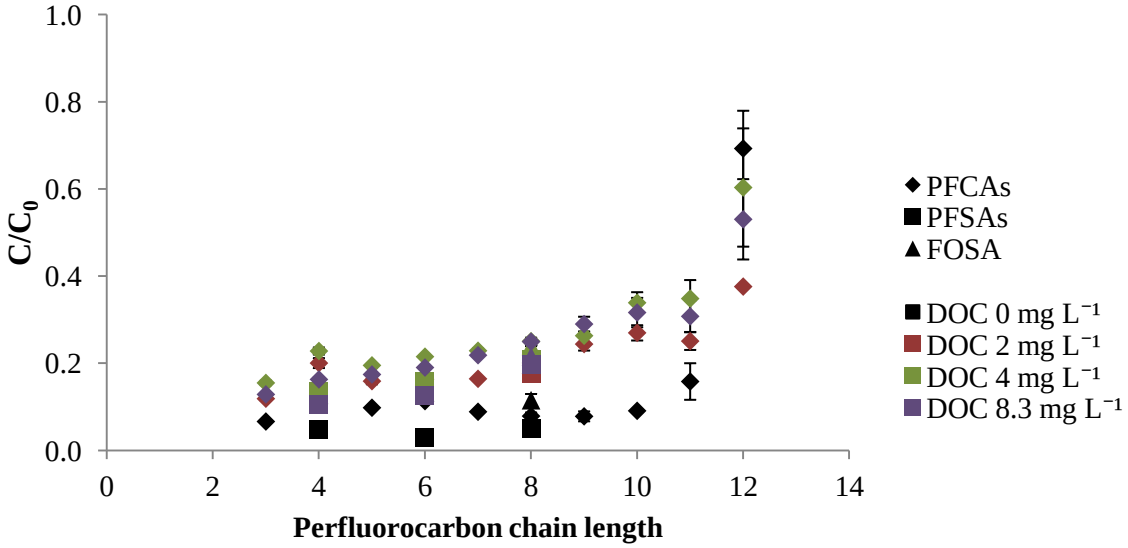

Figure 23. Correlation between perfluorocarbon chain length and C/C_0 (concentration at the end of the experiment compared to initial concentration) and the influence of DOC concentration, using water from lake Bolmen and AE as adsorbent. Experiments performed in duplicate, standard deviation presented as error bars. The shape of the symbol illustrates the compound or subclass and color illustrate DOC concentration.

5 Discussion

5.1 Pilot-scale column experiments at Bäcklösa DWTP

Comparing GAC and AE, a similar trend was observed evaluating the removal efficiency of PFASs; i.e. increase in removal efficiency as chain length increased. However, the removal efficiency differed comparing the two treatment techniques. Among the short-chained PFCAs, PFOA (C_7) was more efficiently removed using AE (52% after 35 224 BVs) compared to GAC (46% after 33 223 BVs). On the other hand, shorter-chained PFCAs PFPeA (C_4), PFHxA (C_5) and PFHpA (C_6) were more efficiently removed using GAC (24%, 23% and 32% after 33 223 BVs, respectively) compared to AE (15%, -4% and 22% after 35 224 BVs, respectively). However, using both GAC and AE as adsorbents, there was a major drop in removal efficiency of PFPeA (C_4) with a negative removal efficiency ranging between -29% and -68% between 10 813 and 21 576 BVs for GAC (Figure 5a) and -13% and -180% between 12 840 and 26 920 BVs for AE (Figure 9a). This might be due to varying concentrations in the reservoir (Figure A1 in Appendix B) or desorption processes of this compound. In addition, PFBA (C_3) had the lowest removal efficiency of the PFCAs using GAC, reaching negative values for removal efficiency after 23 240 BVs, indicating desorption of this compound (Figure 5a). Desorption of PFBA has been observed earlier, in a leaching experiment on PFASs in soil (Gellrich et al., 2012). As longer-chained and more lipophilic PFASs (PFHxA and PFHxS) were added to the soil, previously added and adsorbed PFBA started to desorb. Gellrich et al. (2012) suggested that the longer-chained PFHxA and PFHxS displaced the shorter-chained PFBA from their binding sites, thus leading to desorption (Gellrich et al., 2012). A similar trend was observed using AE as adsorbent, as PFBA (C_3) and PFHxA (C_5) reached negative values for removal efficiency after 28 996 and 31 078 BVs, respectively, indicating desorption (Figure 9a). As described by Eschauzier et al. (2012) and Gellrich et al. (2012) longer-chained PFASs have shown a tendency to displace shorter-chained PFASs from their binding sites. Higgins and Luthy (2006) also demonstrated higher sorption potential of longer-chained PFASs than their short-chained equivalents, and, in addition, Zhao et al. (2012) indicated that desorption became less difficult as chain length decreased. Furthermore, in this study, long-chained PFCAs (C_8-C_{11}, C_{13}) were more efficiently removed using AE compared to GAC after 35 224 and 33 223 BVs, respectively; >70% compared to >55% (Figure 5b; Figure 9b).

In addition, FOSA and the investigated PFSAs were more efficiently removed by AE compared to GAC after 35 224 BVs and 33 223 BVs, respectively; (FOSA: 81% vs 69%, respectively; PFOS (C_8): 97% vs 72%, respectively; PFHxS (C_6): 91% vs 57%, respectively; PFBS (C_4): 68% vs 39%, respectively) (Figure 6a; Figure 10a; Figure 6b; Figure 10b). However, similarly to PFPeA (C_4), the removal efficiency of PFBS (C_4) decreased rapidly, ranging between 13% and 47%, between 10 813 and 21 576 BVs, using GAC as adsorbent (Figure 6b). A similar decrease was observed for PFBS during the same time interval using AE as adsorbent (Figure 10b). The rapid decrease could be described by desorption processes of these short-chain compounds, as suggested by Gellrich et al. (2012). Additionally, the decrease could be caused by fluctuations in the reservoir tank (Figure A1 in Appendix B) in combination with the higher water solubility of these short-chained compounds (Table 1). As the concentration in the water from the reservoir tank decreased, adsorbed compounds might have desorbed due to the concentration differences between solid phase (adsorbent) and water phase, resulting in

higher desorption of compounds with higher water solubility. Another possible explanation is that the major drop of removal efficiency of PFPeA (C_4) and PFBS (C_4) could be due to an increase in flow rate through the column during this period. As the flow rate increase, the contact time between the molecules and the adsorbent decrease, leading to less time during which the molecules can adsorb. Since longer-chained PFASs have higher sorption potential than their short-chained equivalents (Higgins and Luthy, 2006), the longer-chained PFASs might have been preferentially sorbed comparing to the short-chained PFASs, e.g. PFPeA and PFBS, during this period.

Previous studies on PFAS removal indicated similar results in GAC removal efficiency (Senevirathna et al., 2010; Takagi et al., 2011; Chularueangaksorn et al., 2013; Appleman et al., 2014). In a pilotscale-column study using Filtrasorb 400® and 1.3 minute retention time, PFOS was removed >80% the first 40 days, and removal efficiency thereafter decreased to approximately 70% after 60 days (Senevirathna et al., 2010). Takagi et al. (2011) observed a similar trend using two different activated carbon filters in a DWTP. During their study, the removal efficiency of PFOS and PFOA was 100% during the first 100 days, and thereafter the efficiency decreased to approximately 65% after 200 days. Average flow rate thorugh the filter was 1.5×10^6 L day^{-1} and the mass of activated carbon was 1.2×10^7 g (Takagi et al., 2011). During a 117 day long column experiment, Chularueangaksorn et al. (2013) concluded that AE was most efficient removing PFOA using AE (PFA300) compared to GAC (Filtrasorb 400®). AE treated 119 880 BVs of water before a 90% breakthrough point was reached, whereas GAC treated 55 080 BVs before reaching the limit (Chularueangaksorn et al., 2013). In addition, one full-scale study on AE removal efficiency has been performed by Appleman et al. (2014). Using a six minutes hydraulic retention time, a strongly basic AE resin was shown to moderately remove C_6 and C_7 PFCAs (76% for PFOA and 54% for PFHpA), while the removal efficiency for PFSAs was high (>90%, >97% and 83% for PFOS, PFHxS and PFBS, respectively). The removal efficiency of short-chain PFCAs (PFBA, PFHxA and PFPeA) was low or nonexistant (Appleman et al., 2014).

In this study, both GAC and AE displayed increased removal efficiency of PFSAs and PFCAs with increasing chain length. In addition, PFSAs had higher removal efficiency than PFCAs, comparing the same number of perfluorocarbons in the chain length (56% vs 38% for GAC, respectively, and 82% vs 28% for AE, respectively) (Figure 8; Figure 12). Higher sorption potential with increasing chain length and higher adsorption of sulfonates compared to carboxylic groups has been observed in previous studies (Higgins and Luthy, 2006; Ahrens et al., 2009b; McCleaf, 2013). Due to that PFSAs are stronger acids and more hydrophobic compared to PFCAs, their tendency to adsorb is higher (Du et al., 2014). However, as suggested by negative removal efficiencies for C_3 (PFBA), C_4 (PFPeA) and C_5 (PFHxA) in figure 8 and figure 12, PFASs cannot be formed under these conditions. The negative removal efficiencies observed could be due to fluctuations in the reservoir tank (Figure A1 in Appendix B) or that sampling was limited to approximately once a week, possibly introducing errors when estimating the concentrations before and after GAC or AE treatment.

The adsorption of PFASs in μg g^{-1} adsorbent (both GAC and AE) generally increased with increasing number of BVs (Figure 7; Figure 11), indicating that the maximum adsorption capacity for most investigated PFASs have not yet been reached during this

Master thesis. However, for PFBA in the GAC column and both PFBA and PFHxA in the AE column, the adsorption g^{-1} adsorbent had levelled off and started to decrease, i.e. desorb. This phenomen can be explained by displacement off short-chained PFASs by long-chained PFASs, as reported by Eschauzier et al. (2012) and Gellrich et al. (2012) in previous studies. In addition, adsorption of PFPeA decreased after 10 813 and 12 840 BVs for GAC and AE respectively, followed by an increase six sampling points later. The underlying mechanism is, however, not fully understood. One possible explanation could be fluctuations of the PFAS concentrations in the reservoir tank (Figure A1 in Appendix B). Furthermore, as suggested by Higgins and Luthy (2006), longer-chained PFASs have higher sorption potential than their short-chain equivalants. In contrast, the results presented in figure 7 and figure 11 suggests differently, e.g. PFTeDA (C_{13}) had the lowest adsorption ($\mu g\ g^{-1}$ adsorbent) among the long-chained PFCAs using both GAC and AE. However, the results reflect the average concentration in the reservoir tank, as PFTeDA was present in the lowest concentrations (15±19 ng L^{-1}) compared to the other investigated long-chain PFCAs (Table A3 in Appendix B).

When AE was used as adsorbent, both linear and branched PFOS, FOSA and PFHxS were removed equally efficient (Figure 13a; Figure 14a; Figure 15a). In contrast, linear PFOS, FOSA and PFHxS were more efficiently removed than their isomers using GAC (Figure 13b; Figure 14b; Figure 15b). Similar results have been observed by Eschauzier et al. (2012), where linear isomers of PFOS and PFOA were preferentially sorbed to GAC compared to their branched isomers. Early studies on the behavior of isomers during sorption onto activated carbon indicated decreasing sorption capacity with increasing degree of branching (Belfort, 1979; Eschauzier et al., 2012). A possible explanation could be a generally smaller molecular volume of branched isomers, resulting in a smaller gain in Gibbs free energy from adsorption compared to linear isomers (Wang et al., 2011). However, as removal efficiency for PFOS, FOSA and PFHxS was similar for both linear and branched isomers using AE as adsorbent, another sorption mechanism seems to have caused the observed differences in removal efficiency for AE. Hydrophobic interaction and electrostatic interactions are the two primary mechanisms for removal using AE (Rahman et al., 2014), and the results indicate similar hydrophobicity and similar ionic strength of both linear and branched PFOS, FOSA and PFHxS.

As described above, shorter-chained PFCAs (C_4-C_6) were more efficiently removed using GAC compared to AE after 33 223 and 35 224 BVs, respectively. On the other hand, PFOA (C_7), long-chained PFCAs (C_8-C_{11}, C_{13}), FOSA and PFSAs were more efficiently removed by AE than GAC during the same period. However, to determine which technique is most suitable for full-scale applications there are other factors, both economic and technical, than removal efficiency to consider. The column-study was performed during 140 days, whereas DWTP applies the technique for a longer period of time. As the removal efficiency of the investigated adsorbents decrease over time and with increasing number of BVs, regeneration of the adsorbents is needed (Takagi et al., 2011). Filtrasorb 400® is regenerated using thermal reactivation; a high temperature reaction using steam, destroying the organic compounds adsorbed and restoring the adsorption capacity of the GAC (Calgon Carbon Corporation, 2012). Purolite A-600 is on the other hand, regenerated using e.g. NaCl, NaOH and methanol, desorbing the adsorbed PFASs via ion exchange (Deng et al., 2010). The disposal of the PFAS concentrate resulting from AE regeneration is another issue to be addressed (Rahman et al., 2014).

In addition, each water type has specific conditions, e.g. DOC content, pH and chemical parameters, such as content of sulphate ions (SO_4^{2-}) which has to be taken into consideration (Table A1 in Appendix A). The presence of sulphate ions (which was 40 and 41 mg L^{-1} in the reservoir tank, day 3 and 48, respectively) has been shown to decrease the sorption capacity of PFOS onto two AE resins (IRA67 and IRA958), however, not to a similar extent, indicating that resin properties also affects the sorption capacity (Deng et al., 2010). In addition, pH was shown to affect the sorption capacity of the two AE resins (Deng et al., 2010). However, Purolite A-600 used in this study, does not have any pH limitations (Purolite, 2012). As suggested by Rahman et al. (2014), DOC might influence the adsorption to GAC, as GAC might be saturated faster when DOC is present, or DOC might compete with PFASs during sorption to GAC, thus reducing the adsorption of PFASs (Rahman et al., 2014). In this study, adsorption of DOC occurred in the GAC column, with a parallel adsorption of both PFASs and DOC (Figure 24). During this column-study both DOC and PFASs seemed to adsorb continously over time, with no reduction in either DOC or most PFAS adsorption (except PFBA and PFPeA in the GAC column and PFBA, PFHxA and PFPeA in the AE column). Further investigation on DOC effect on AE and GAC was performed during batch experiments included in this Master thesis.

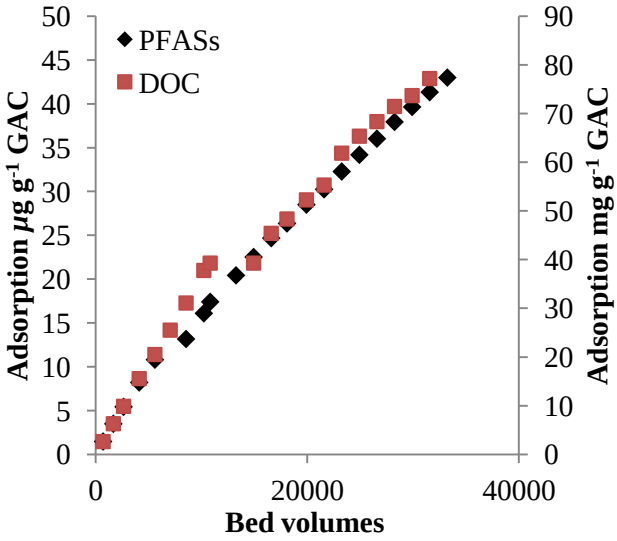

Figure 24. Adsorption of PFASs and DOC in the GAC column. The adsorption of PFASs is displayed as μg g^{-1} GAC, whereas adsorption of DOC is displayed in mg g^{-1} GAC.

5.2 Laboratory batch experiments

Using GAC as adsorbent, the adsorption of PFASs generally increased with increasing DOC in the water (Figure 16; Figure 18), indicating that DOC enhanced the PFAS sorption onto GAC. Furthermore, the effect of different DOC concentrations differed depending on water type. For example, comparing water from lake Görväln and lake Bolmen, the general trend for short-chain PFCAs (C_4-C_7) using water from lake Görväln was a larger increase in sorption at DOC concentrations 4 and 8.3 mg L^{-1} compared to 2 mg L^{-1} (Figure 16), whereas experiments using water from lake Bolmen resulted in higher (and similar) sorption than DOC 0 mg L^{-1} for all DOC concentration, regardless of concentration (Figure 18). The mechanism contributing to enhanced PFAS sorption onto GAC in presence of DOC is not fully understood. One possible explanation could be formation of biofilm on the GAC surface as DOC is present, contributing to increased adsorption of PFASs to the surface. In contrast to the results showing increasing adsorption of PFASs to GAC in the presence of DOC, adsorption of PFASs to AE generally decreased with increasing DOC concentration (Figure 20; Figure 22). In water from lake Görväln, all DOC concentrations generally resulted in a similar decrease in adsorption capacity, whereas DOC concentration 4 mg L^{-1} caused the largest decrease in adsorption capacity using water from lake Bolmen. In contrast to GAC, for AE

hydrophobic interaction and electrostatic interactions are two primary mechanisms for removal of PFASs (Rahman et al., 2014). Decreased adsorption onto AE when DOC was present could possibly be explained by occupation of pore space and adsorption sites by DOC, resulting in fewer sites where PFASs can adsorb.

Few studies have been performed on the effects of DOC on PFAS removal efficiency, and the ones performed indicate, contrary to the results from this study, decreasing adsorption of PFASs to GAC and increasing adsorption of PFASs to AE with increasing DOC (Dudley, 2012; Appleman et al., 2013). During rapid small-scale column tests with an EBCT of 0.38 min, Appleman et al. (2013) evaluated the effect of DOC (1.7 mg L^{-1}) on the removal efficiency of C_3-C_5, C_7-C_9 PFCAs and C_4-C_8 PFSAs using three types of GAC (Filtrasorb 300®, Filtrasorb 600® and Siemens AquaCarb® 1240C). The results indicated faster break-through of all PFASs when DOC was present. The authors hypothesize that organic matter occupied sorption sites or pore space (Appleman et al., 2013). Similar results have been observed studying other organic compounds; reduced removal efficiency of pesticides using GAC (Filtrasorb 400® and Picabiol), due to competition for adsorption sites, has been observed in the presence of NOM (Matsui et al., 2002). Furthermore, the results from experiments performed during a Master thesis by Dudley (2012) indicated increased adsorption of PFASs (C_3-C_9 PFCAs and C_4-C_8 PFSAs) to three strong base AE resins and one weak base AE resin (manufacturing names not provided) when natural organic matter (NOM) was present (4.5 mg L^{-1}). Two hypotheses were discussed; either PFAS associated with NOM were physically drawn into the resin matrix, or NOM coating of the resin altered the resin surface, increasing the affinity of PFASs. The first hypothesis was tested; preloading 5 mL L^{-1} resin matrix with NOM for 24 hours before spiking was performed. However, no or little reduction in PFAS concentration was observed. The second theory was, however, not tested, resulting in a need for further evaluation of this hypothesis (Dudley, 2012). The reason behind the different results between this study and the previously performed studies by Dudley (2012) and Appleman et al. (2013) is not clear. Possible reasons could be potential presence of anions in the lake water used during the experiments, also competing for active sites. In addition, sodium bicarbonate was added to the water as buffer to reduce pH effects, forming carbonate and bicarbonate ions which also potentially could compete for active sites, especially on the AE.

The effect of DOC concentration depending on perfluorocarbon chain length is also shown in figures 17 and 19 (GAC) and figure 21 and 23 (AE). For water from both lake Görväln and lake Bolmen, regardless of DOC concentration in the water, adsorption decreased with increasing perfluorocarbon chain length, in contrast to previous studies were adsorption on the other hand increases with perfluorocarbon chain length (Higgins and Luthy, 2006; Ahrens et al., 2009b). The mechanism possibly causing this trend is not clear, however, Du et al. (2014) reported on studies indicating a weaker steric effect and faster diffusion of smaller PFAS molecules into porous AE resins compared to larger PFAS molecules, resulting in faster adsorption kinetics and possibly a higher amount adsorbed (Du et al., 2014). Possibly, this might also be the mechanism for diffusion into porous GAC particles. In addition, the equilibration times for long-chained PFASs are longer. A study by Englund (2015) showed that equilibrium was reached after 5-10 hours for short-chain PFCAs (C_3-C_7) while long-chain PFCAs (C_8-C_{13}) reached equilibrium after 10-24 hours using AE (Purolite A-600) (Englund, 2015). The batch experiments in

this study were performed during 15 minutes, indicating non-equilibrium conditions, possibly explaining the stronger sorption of shorter-chained PFASs.

The results also indicated differences in sorption capacity depending on which water type was used. Figure 25 illustrates how adsorption of the investigated C_8 PFASs´ (PFNA, FOSA and PFOS) differed depending on DOC concentration and water type. Comparing both water types, adsorption of the investigated C_8 PFASs onto GAC increased more rapidly with increasing DOC concentration using water from lake Görväln compared to lake Bolmen, resulting in average C/C_0 0.10 and 0.38 at DOC concentration 8.3 mg L^{-1}, respectively (Figure 25). In addition, the C_8 PFASs were also more efficiently removed in water from lake Görväln compared to lake Bolmen using AE as adsorbent (average C/C_0 for 2 mg L^{-1} was 0.13 and 0.19, respectively; for 4 mg L^{-1} 0.15 and 0.23, respectively; for 8.3 mg L^{-1} 0.15 and 0.22, respectively). Thus, the results indicated higher adsorption of PFASs to both GAC and AE using water from lake Görväln compared to lake Bolmen.

The two water types have different DOC characteristics; the organic carbon in lake Görväln is mainly autochthonous; i.e. hydrophilic material produced by bacteria and algae within the lake, while the organic carbon in lake Bolmen mainly is hydrophobic material with terrestrial origin and thus is allochthonous. As suggested by Rahman et al. (2014), the two primary mechanisms for PFAS removal are proposed to be adsorption via hydrophobic interactions and electrostatic interactions. Since DOC from lake Bolmen is more hydrophobic, it might be more competitive for available adsorption sites compared to the hydrophilic DOC present in water from lake Görväln. Thus, the sorption of PFASs to GAC and AE was lower using water from lake Bolmen compared to water from lake Görväln. Furthermore, depending on origin, DOC characteristics vary; DOC produced by algae and bacteria has relatively high nitrogen content and low content of phenols and aromatic carbon, while DOC with terrestrial origin have relatively low nitrogen content and high content of phenols and aromatic carbon (Fabris et al., 2008). The aromatic carbon is considered a major reactive component in DOC (Fabris et al., 2008), possibly resulting in higher reactivity of terrestrial DOC from lake Bolmen compared to aquatic DOC from lake Görväln. This might lead to a higher degree of interaction between terrestrial DOC from lake Bolmen and the GAC or AE, occupying more pore space or adsorption sites. Thus, the result would be lower PFAS sorption to GAC and AE when water from lake Bolmen was used, compared to water from lake Görväln.

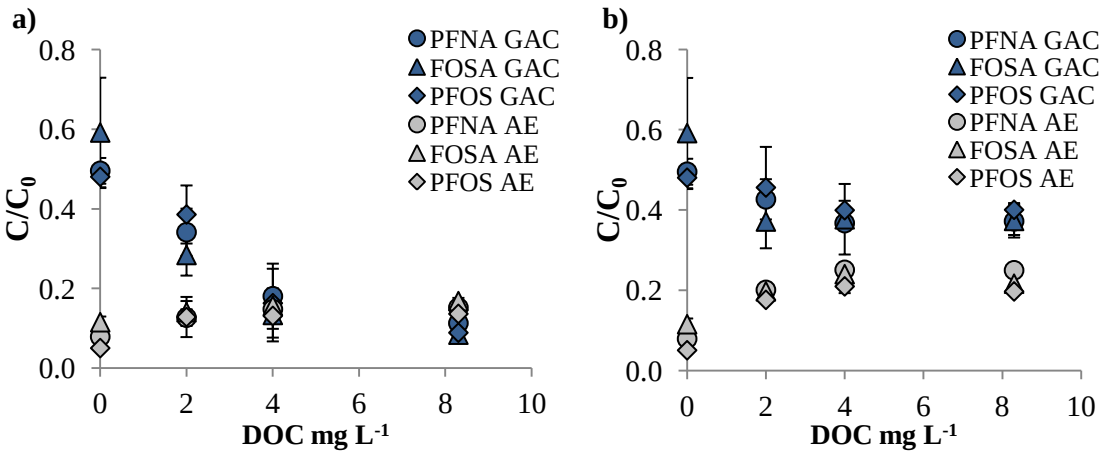

Figure 25. C/C_0 for investigated C_8 PFASs (PFNA, FOSA and PFOS) based on DOC concentration in water for a) lake Görväln and b) lake Bolmen.

6 Conclusion

The results in the column experiments indicated a decrease in removal efficiency with increasing number of BVs for both GAC and AE. Short-chained PFCAs (PFPeA (C_4), PFHxA (C_5) and PFHpA (C_6)) were more efficiently removed using GAC compared to AE. On the other hand, AE was more efficient than GAC removing long-chained PFCAs (C_8-C_{11}, C_{13}), FOSA and the studied PFSAs. The column experiment also resulted in differences in removal efficiency comparing linear and branched PFOS, FOSA and PFHxS. Branched isomers were less efficienctly removed by GAC compared to the linear isomers, while however, AE removed both branched and linear isomers equally efficient.

The column experiment resulted in higher removal efficiency of PFSAs than PFCAs, comparing the same number of carbons in the perfluorocarbon chain length. Thus, the results indicated that functional group affects the removal efficiency of PFASs; sulfonic group resulted in higher removal efficiency compared to carboxylic group, in agreement with the first hypothesis of this study. Similar results have been observed in previous studies (Higgins and Luthy, 2006; Ahrens et al., 2009b; McCleaf, 2013).

The removal efficiency of GAC and AE was, in addition, influenced by the length of the perfluorocarbon chain, in accordance with the first hypothesis. The results from the column experiments indicated higher removal efficiency of PFSAs and PFCAs as the perfluorocarbon chain length increased, as observed during previous studies (Higgins and Luthy, 2006; Ahrens et al., 2009b; McCleaf, 2013). However, the results from the batch experiments showed the opposite; decreasing adsorption to GAC and AE as the chain length increased. The possible mechanism is not fully understood, however, previous studies indicated weaker steric effect and faster diffusion of smaller PFAS molecules into the pores of the resin, compared to larger molecules (Du et al., 2014).

The presence of DOC in the water affected the removal efficiency of PFASs, in agreement with the second hypothesis. However, the results indicated, contrary to the few studies previously performed on DOC and removal efficiency, enhanced sorption of PFASs to GAC with increasing DOC concentration, and decreased PFAS sorption to AE as the DOC concentration increased, with a contact time of 15 minutes. In addition, the removal efficiency of GAC and AE varied using water types with different DOC origin, indicating that DOC characteristics influence the sorption capacity of the adsorbents.

The average removal efficiency of all PFASs during the 140 day column study was 65% for both GAC and AE. However, the removal efficiency of the investigated PFASs was lowest for short-chained PFCAs (C_3-C_6) using both GAC and AE (ranging between -12% and 32% after 33 223 BVs and -8.1% and 22% after 35 224 BVs, respectively). The phase-out of PFOS, PFOA and related long-chained substances results in replacement with (most often) shorter chained PFASs (Wang et al., 2009). In addition, the drinking water in Uppsala has shown to be contaminated with mostly short-chained PFASs such as PFBS (C_4) and PFHxS (C_6) (Livsmedelsverket, 2012), resulting in that further studies are needed focusing on removal of short-chained PFASs. In addition, the results in this study indicate a complicated correlation between PFAS removal and the presence and characteristics of DOC, an area which also requires further studies.

7 References

AHRENS, L. 2011. Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate. *Journal of Environmental Monitoring,* 13**,** 20-31.

AHRENS, L., BARBER, J. L., XIE, Z. & EBINGHAUS, R. 2009a. Longitudinal and Latitudinal Distribution of Perfluoroalkyl Compounds in the Surface Water of the Atlantic Ocean. *Environmental Science & Technology,* 43**,** 3122-3127.

AHRENS, L., HARNER, T., SHOEIB, M., LANE, D. A. & MURPHY, J. G. 2012. Improved Characterization of Gas–Particle Partitioning for Per- and Polyfluoroalkyl Substances in the Atmosphere Using Annular Diffusion Denuder Samplers. *Environmental Science & Technology,* 46**,** 7199-7206.

AHRENS, L., SHOEIB, M., HARNER, T., LEE, S. C., GUO, R. & REINER, E. J. 2011. Wastewater Treatment Plant and Landfills as Sources of Polyfluoroalkyl Compounds to the Atmosphere. *Environmental Science & Technology,* 45**,** 8098-8105.

AHRENS, L., TANIYASU, S., YEUNG, L. W. Y., YAMASHITA, N., LAM, P. K. S. & EBINGHAUS, R. 2010. Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. *Chemosphere,* 79**,** 266-272.

AHRENS, L., YAMASHITA, N., YEUNG, L. W. Y., TANIYASU, S., HORII, Y., LAM, P. K. S. & EBINGHAUS, R. 2009b. Partitioning Behavior of Per- and Polyfluoroalkyl Compounds between Pore Water and Sediment in Two Sediment Cores from Tokyo Bay, Japan. *Environmental Science & Technology,* 43**,** 6969-6975.

ALTMANN, J., RUHL, A. S., ZIETZSCHMANN, F. & JEKEL, M. 2014. Direct comparison of ozonation and adsorption onto powdered activated carbon for micropollutant removal in advanced wastewater treatment. *Water Research,* 55**,** 185-193.

APPLEMAN, T. D., DICKENSON, E. R. V., BELLONA, C. & HIGGINS, C. P. 2013. Nanofiltration and granular activated carbon treatment of perfluoroalkyl acids. *Journal of Hazardous Materials,* 260**,** 740-746.

APPLEMAN, T. D., HIGGINS, C. P., QUIÑONES, O., VANDERFORD, B. J., KOLSTAD, C., ZEIGLER-HOLADY, J. C. & DICKENSON, E. R. V. 2014. Treatment of poly- and perfluoroalkyl substances in U.S. full-scale water treatment systems. *Water Research,* 51**,** 246-255.

BELFORT, G. 1979. Selective adsorption of organic homologues onto activated carbon from dilute aqueous solutions. Solvophobic interaction approach and correlations of molar adsorptivity with physicochemical parameters. *Environmental Science & Technology,* 13**,** 939-946.

BHHATARAI, B. & GRAMATICA, P. 2010. Prediction of Aqueous Solubility, Vapor Pressure and Critical Micelle Concentration for Aquatic Partitioning of Perfluorinated Chemicals. *Environmental Science & Technology,* 45**,** 8120-8128.

BORG, D. & HÅKANSSON, H. 2012. Environmental and health risk assessment of perfluoroalkylated and polyfluoroalkylated substances (PFASs) in Sweden. Report 6513, Swedish Environmental Protection Agency.

BUCK, R. C., FRANKLIN, J., BERGER, U., CONDER, J. M., COUSINS, I. T., DE VOOGT, P., JENSEN, A. A., KANNAN, K., MABURY, S. A. & VAN LEEUWEN, S. P. J. 2011. Perfluoroalkyl and polyfluoroalkyl substances in the environment: Terminology, classification, and origins. *Integrated Environmental Assessment and Management,* 7**,** 513-541.

CALGON CARBON CORPORATION 2012. Filtrasorb®400 - Granular activated carbon for municipal specifications. Calgon Carbon Corporation. Pittsburgh, USA.

CHULARUEANGAKSORN, P., TANAKA, S., FUJII, S. & KUNACHEVA, C. 2013. Adsorption of perfluorooctanoic acid (PFOA) onto anion exchange resin, non-ion exchange resin, and granular-activated carbon by batch and column. *Desalination and Water Treatment,* 52**,** 6542-6548.

CRITTENDEN, J. C., TRUSSELL, R. R., HAND, D. W., HOWE, K. J. & TCHOBANOGLOUS, G. 2012a. Adsorption. *MWH's Water Treatment: Principles and Design, Third Edition.* John Wiley & Sons, Inc.

CRITTENDEN, J. C., TRUSSELL, R. R., HAND, D. W., HOWE, K. J. & TCHOBANOGLOUS, G. 2012b. Ion Exchange. *MWH's Water Treatment: Principles and Design, Third Edition.* John Wiley & Sons, Inc.

D'HOLLANDER, W., DE VOOGT, P., DE COEN, W. & BERVOETS, L. 2010. Perfluorinated Substances in Human Food and Other Sources of Human Exposure. *In:* DE VOOGT, P. (ed.) *Reviews of Environmental Contamination and Toxicology Volume 208.* Springer New York.

DENG, S., YU, Q., HUANG, J. & YU, G. 2010. Removal of perfluorooctane sulfonate from wastewater by anion exchange resins: Effects of resin properties and solution chemistry. *Water Research,* 44**,** 5188-5195.

DU, Z., DENG, S., BEI, Y., HUANG, Q., WANG, B., HUANG, J. & YU, G. 2014. Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents—A review. *Journal of Hazardous Materials,* 274**,** 443-454.

DUDLEY, L.-A. M. B. 2012. Removal of perfluorinated compounds by powdered activated carbon, superfine powdered activated carbon, and anion exchange resins. Master thesis; Graduate Faculty of North Carolina State University. Raleigh, North Carolina.

ENGLUND, S. 2015. Evaluation of the removal efficiency of perfluoroalkyl substances in drinking water. Master thesis; Uppsala University and Swedish University of Agricultural Sciences. Uppsala.

ENVIRONMENT CANADA. 2010. *Environmental performance agreements regarding perfluorinated carboxylic acids (PFCAs) and their precursors (2010-2015)* [Online]. Available: http://ec.gc.ca/epe-epa/default.asp?lang=En&n=0D8C879E-1 [Accessed June 2 2015].

ERICSON, I., DOMINGO, J., NADAL, M., BIGAS, E., LLEBARIA, X., VAN BAVEL, B. & LINDSTRÖM, G. 2009. Levels of Perfluorinated Chemicals in Municipal Drinking Water from Catalonia, Spain: Public Health Implications. *Archives of Environmental Contamination and Toxicology,* 57**,** 631-638.

ESCHAUZIER, C., BEERENDONK, E., SCHOLTE-VEENENDAAL, P. & DE VOOGT, P. 2012. Impact of Treatment Processes on the Removal of Perfluoroalkyl Acids from the Drinking Water Production Chain. *Environmental Science & Technology,* 46**,** 1708-1715.

EUROPEAN PARLIAMENT 2006. Directive 2006/122/EC of the European Parliament and of the Council of 12 December 2006. Official Journal of the EU, 27 December 2006, L372/32-L372/34.

FABRIS, R., CHOW, C. W. K., DRIKAS, M. & EIKEBROKK, B. 2008. Comparison of NOM character in selected Australian and Norwegian drinking waters. *Water Research,* 42**,** 4188-4196.

FILELLA, M. 2009. Freshwaters: which NOM matters? *Environmental Chemistry Letters,* 7**,** 21-35.

FLORES, C., VENTURA, F., MARTIN-ALONSO, J. & CAIXACH, J. 2013. Occurrence of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in N.E. Spanish surface waters and their removal in a drinking water treatment plant that combines conventional and advanced treatments in parallel lines. *Science of The Total Environment,* 461–462**,** 618-626.

GELLRICH, V., STAHL, T. & KNEPPER, T. P. 2012. Behavior of perfluorinated compounds in soils during leaching experiments. *Chemosphere,* 87**,** 1052-1056.

GIESY, J. P. & KANNAN, K. 2001. Global Distribution of Perfluorooctane Sulfonate in Wildlife. *Environmental Science & Technology,* 35**,** 1339-1342.

GLYNN, A., BERGER, U., BIGNERT, A., ULLAH, S., AUNE, M., LIGNELL, S. & DARNERUD, P. O. 2012. Perfluorinated Alkyl Acids in Blood Serum from Primiparous Women in Sweden: Serial Sampling during Pregnancy and Nursing, And Temporal Trends 1996–2010. *Environmental Science & Technology,* 46**,** 9071-9079.

HIGGINS, C. P. & LUTHY, R. G. 2006. Sorption of Perfluorinated Surfactants on Sediments†. *Environmental Science & Technology,* 40**,** 7251-7256.

HOFFMAN, K., WEBSTER, T. F., BARTELL, S. M., WEISSKOPF, M. G., FLETCHER, T. & VIEIRA, V. M. 2010. Private Drinking Water Wells as a Source of Exposure to Perfluorooctanoic Acid (PFOA) in Communities Surrounding a Fluoropolymer Production Facility.

JEON, J., KANNAN, K., LIM, B. J., AN, K. G. & KIM, S. D. 2011. Effects of salinity and organic matter on the partitioning of perfluoroalkyl acid (PFAs) to clay particles. *Journal of Environmental Monitoring,* 13**,** 1803-1810.
JÄRNBERG, U., HOLMSTRÖM, K., VAN BAVEL, B. & KÄRRMAN, A. 2006. Perfluoroalkylated acids and related compounds (PFAS) in the Swedish environment - Chemistry, sources, exposure. Stockholm University & Örebro University.
KANNAN, K., CORSOLINI, S., FALANDYSZ, J., FILLMANN, G., KUMAR, K. S., LOGANATHAN, B. G., MOHD, M. A., OLIVERO, J., WOUWE, N. V., YANG, J. H. & ALDOUS, K. M. 2004. Perfluorooctanesulfonate and Related Fluorochemicals in Human Blood from Several Countries. *Environmental Science & Technology,* 38**,** 4489-4495.
LAMPERT, D. J., FRISCH, M. A. & SPEITEL JR, G. E. 2007. Removal of Perfluorooctanoic Acid and Perfluorooctane Sulfonate from Wastewater by Ion Exchange. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management,* 11**,** 60-68.
LAU, C., ANITOLE, K., HODES, C., LAI, D., PFAHLES-HUTCHENS, A. & SEED, J. 2007. Perfluoroalkyl Acids: A Review of Monitoring and Toxicological Findings. *Toxicological Sciences,* 99**,** 366-394.
LINDSTROM, A. B., STRYNAR, M. J. & LIBELO, E. L. 2011. Polyfluorinated Compounds: Past, Present, and Future. *Environmental Science & Technology,* 45**,** 7954-7961.
LIVSMEDELSVERKET 2012. Riskvärdering. Perfluorerade alkylsyror (PFAA) i Uppsalas dricksvatten. Diarienummer 1192/2012.
LIVSMEDELSVERKET 2013. Riskvärdering av perfluorerade alkylsyror i livsmedel och dricksvatten. Rapport 11.
MACHENBACH, I. 2007. Drinking water production by coagulation and membrane filtration. Trondheim: Norwegian University of Science and Technology, Faculty of Engineering Science and Technology, Department of Hydraulic and Environmental Engineering.
MARTIN, J. W., MABURY, S. A., SOLOMON, K. R. & MUIR, D. C. G. 2003. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (Oncorhynchus mykiss). *Environmental Toxicology and Chemistry,* 22**,** 196-204.
MATSUI, Y., KNAPPE, D. R. U. & TAKAGI, R. 2002. Pesticide Adsorption by Granular Activated Carbon Adsorbers. 1. Effect of Natural Organic Matter Preloading on Removal Rates and Model Simplification. *Environmental Science & Technology,* 36**,** 3426-3431.
MCCLEAF, P. 2013. Reduction of PFAA in drinking water with active carbon filtration and ion exchange. Presentation at the Swedish Drinking Water Conference April 18, 2013. Gothenburg, Sweden.
MOODY, C. A., HEBERT, G. N., STRAUSS, S. H. & FIELD, J. A. 2003. Occurrence and persistence of perfluorooctanesulfonate and other perfluorinated surfactants in groundwater at a fire-training area at Wurtsmith Air Force Base, Michigan, USA. *Journal of Environmental Monitoring,* 5**,** 341-345.
NAKAYAMA, S. F., STRYNAR, M. J., REINER, J. L., DELINSKY, A. D. & LINDSTROM, A. B. 2010. Determination of Perfluorinated Compounds in the Upper Mississippi River Basin. *Environmental Science & Technology,* 44**,** 4103-4109.
OCHOA-HERRERA, V. & SIERRA-ALVAREZ, R. 2008. Removal of perfluorinated surfactants by sorption onto granular activated carbon, zeolite and sludge. *Chemosphere,* 72**,** 1588-1593.
OWEN, D. M., AMY, G. L., CHOWDHURY, Z. K., RAJENDRA, P., GEORGE, M. & KATHY, V. 1995. NOM characterization and treatability. *American Water Works Association***,** 46-63.
POST, G. B., COHN, P. D. & COOPER, K. R. 2012. Perfluorooctanoic acid (PFOA), an emerging drinking water contaminant: A critical review of recent literature. *Environmental Research,* 116**,** 93-117.
POST, G. B., LOUIS, J. B., COOPER, K. R., BOROS-RUSSO, B. J. & LIPPINCOTT, R. L. 2009. Occurrence and Potential Significance of Perfluorooctanoic Acid (PFOA) Detected in New Jersey Public Drinking Water Systems. *Environmental Science & Technology,* 43**,** 4547-4554.
PREVEDOUROS, K., COUSINS, I. T., BUCK, R. C. & KORZENIOWSKI, S. H. 2005. Sources, Fate and Transport of Perfluorocarboxylates. *Environmental Science & Technology,* 40**,** 32-44.
PUROLITE 2012. Purolite® A600. Gel Type 1 strong base anion exchange resin.

QUIÑONES, O. & SNYDER, S. A. 2009. Occurrence of Perfluoroalkyl Carboxylates and Sulfonates in Drinking Water Utilities and Related Waters from the United States. *Environmental Science & Technology,* 43**,** 9089-9095.

RAHMAN, M. F., PELDSZUS, S. & ANDERSON, W. B. 2014. Behaviour and fate of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in drinking water treatment: A review. *Water Research,* 50**,** 318-340.

RAYNE, S. & FOREST, K. 2009. Perfluoroalkyl sulfonic and carboxylic acids: A critical review of physicochemical properties, levels and patterns in waters and wastewaters, and treatment methods. *Journal of Environmental Science and Health, Part A,* 44**,** 1145-1199.

SENEVIRATHNA, S. T. M. L. D., TANAKA, S., FUJII, S., KUNACHEVA, C., HARADA, H., ARIYADASA, B. H. A. K. T. & SHIVAKOTI, B. R. 2010. Adsorption of perfluorooctane sulfonate (n-PFOS) onto non ion-exchange polymers and granular activated carbon: Batch and column test. *Desalination,* 260**,** 29-33.

SEPULVADO, J. G., BLAINE, A. C., HUNDAL, L. S. & HIGGINS, C. P. 2011. Occurrence and Fate of Perfluorochemicals in Soil Following the Land Application of Municipal Biosolids. *Environmental Science & Technology,* 45**,** 8106-8112.

STEINLE-DARLING, E. & REINHARD, M. 2008. Nanofiltration for Trace Organic Contaminant Removal: Structure, Solution, and Membrane Fouling Effects on the Rejection of Perfluorochemicals. *Environmental Science & Technology,* 42**,** 5292-5297.

TAKAGI, S., ADACHI, F., MIYANO, K., KOIZUMI, Y., TANAKA, H., WATANABE, I., TANABE, S. & KANNAN, K. 2011. Fate of Perfluorooctanesulfonate and perfluorooctanoate in drinking water treatment processes. *Water Research,* 45**,** 3925-3932.

ULLAH, S., ALSBERG, T. & BERGER, U. 2011. Simultaneous determination of perfluoroalkyl phosphonates, carboxylates, and sulfonates in drinking water. *Journal of Chromatography A,* 1218**,** 6388-6395.

UN ENVIRONMENTAL PROGRAMME. 2009. *Governments unite to step-up reduction on global DDT reliance and add nine new chemicals under international treaty* [Online]. Available: http://chm.pops.int/Convention/Pressrelease/COP4Geneva8May2009/tabid/542/language/en-US/Default.aspx [Accessed June 2 2015].

UNITED NATIONS ECONOMIC COMMISSION FOR EUROPE. 2009. *Revision of the protocol on persistent organic pollutants. ECE/EB.AIR/2009/9.* [Online]. Available: http://www.unece.org/fileadmin/DAM/env/documents/2009/EB/eb/ece.eb.air.2009.9.e.pdf [Accessed June 2 2015].

US ENVIRONMENTAL PROTECTION AGENCY. 2006. *2010/2015 PFOA Stewardship Program* [Online]. Available: http://www.epa.gov/opptintr/pfoa/pubs/stewardship/ [Accessed June 2 2015].

WANG, T., WANG, Y., LIAO, C., CAI, Y. & JIANG, G. 2009. Perspectives on the Inclusion of Perfluorooctane Sulfonate into the Stockholm Convention on Persistent Organic Pollutants. *Environmental Science & Technology,* 43**,** 5171-5175.

WANG, Z., MACLEOD, M., COUSINS, I. T., SCHERINGER, M. & HUNGERBÜHLER, K. 2011. Using COSMOtherm to predict physicochemical properties of poly- and perfluorinated alkyl substances (PFASs). *Environmental Chemistry,* 8**,** 389-398.

WATER TREATMENT GUIDE. 2007. *Technical database for the water treatment industry. Terminology.* [Online]. Available: http://www.watertreatmentguide.com/terminology_description.htm [Accessed June 4 2015].

YU, Q., ZHANG, R., DENG, S., HUANG, J. & YU, G. 2009. Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: Kinetic and isotherm study. *Water Research,* 43**,** 1150-1158.

ZHAO, L., ZHU, L., YANG, L., LIU, Z. & ZHANG, Y. 2012. Distribution and desorption of perfluorinated compounds in fractionated sediments. *Chemosphere,* 88**,** 1390-1397.

8 Appendix

Appendix A. Properties of water used in the pilot-scale column experiments

Table A1. Chemical parameters of water collected at days 3 and 48 from the reservoir, the GAC column and the AE column. Analysis performed by Uppsala Vatten

Chemical property	Reservoir (day 3)	GAC column (day 3)	AE column (day 3)	Reservoir (day 48)	GAC column (day 48)	AE column (day 48)
°dH	8.5	8.6	8.4	8.9	9.0	8.9
Al^{3+} (mg L^{-1})	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Alkalinity (mg L^{-1})	115	115	129	112	114	112
Ca^{2+} (mg L^{-1})	34.3	34.6	33.2	35.0	35.3	35.1
Cl^{-} (mg L^{-1})	63	63	70	64	64	64
COD Mn (mg L^{-1})	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Conductivity (mS m^{-1})	44.7	47.6	46.8	48.0	48.3	48.1
Cu^{2+} (mg L^{-1})	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
F^{-} (mg L^{-1})	0.91	0.91	0.91	0.97	0.97	0.96
Fe (mg L^{-1})	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mg^{2+} (mg L^{-1})	16.1	16.3	16.3	17.3	17.6	17.3
Mn^{2+} (mg L^{-1})	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Na^{+} (mg L^{-1})	30.4	31.0	30.7	32.4	32.9	32.4
NO_3^{-} (mg L^{-1})	-	-	-	5.0	5.0	5.0
pH	8.3	8.2	8.7	8.2	8.1	8.1
SO_4^{2-} (mg L^{-1})	40	40	15	41	41	42
Turbidity (FNU)	0.18	0.13	0.16	0.12	0.11	0.10
U (µg L^{-1})	30	27	<0.5	33	33	<0.5

Table A2. DOC concentration (mg L^{-1}) in water from the reservoir, the GAC column and the AE column. Analysis performed by Uppsala Vatten

Sampling point	GAC column BVs	AE column BVs	DOC mg L^{-1}		
			Reservoir	GAC column	AE column
Day 3	693	871	1.78	0	0
Day 7	1 661	2 088	1.77	0	0
Day 11	2 629	3 305	1.73	0	0
Day 17	4 106	5 162	1.8	0	1.04
Day 23	5 588	7 025	1.56	0	1.07
Day 29	7 035	8 844	1.62	0	1.16
Day 35	8 533	10 727	1.74	0	1.22
Day 42	10 214	12 840	1.86	0	1.26
Day 46	10 813	13 593	1.74	1.03	1.51
Day 56	13 252	16 534	n.a.	n.a.	n.a.
Day 63	14 915	18 610	n.a.	n.a.	n.a.
Day 70	16 579	20 686	1.67	0	1.44
Day 76	18 070	22 546	1.95	1.05	1.59
Day 84	19 907	24 838	1.99	1.02	1.52
Day 91	21 576	26 920	1.88	1.05	1.46
Day 98	23 240	28 996	1.79	0	1.46
Day 105	24 908	31 078	1.99	1.04	1.46
Day 112	26 567	33 148	1.9	1.08	1.53
Day 119	28 231	35 224	1.88	1.03	1.53
Day 126	29 895	37 300	1.62	1.01	1.37
Day 133	31 554	39 370	1.98	1.02	1.46
Day 140	33 223	41 452	2.23	1.04	1.43

n.a. not available, data missing

Appendix B. Concentration variation in the reservoir used in the pilot-scale column experiment

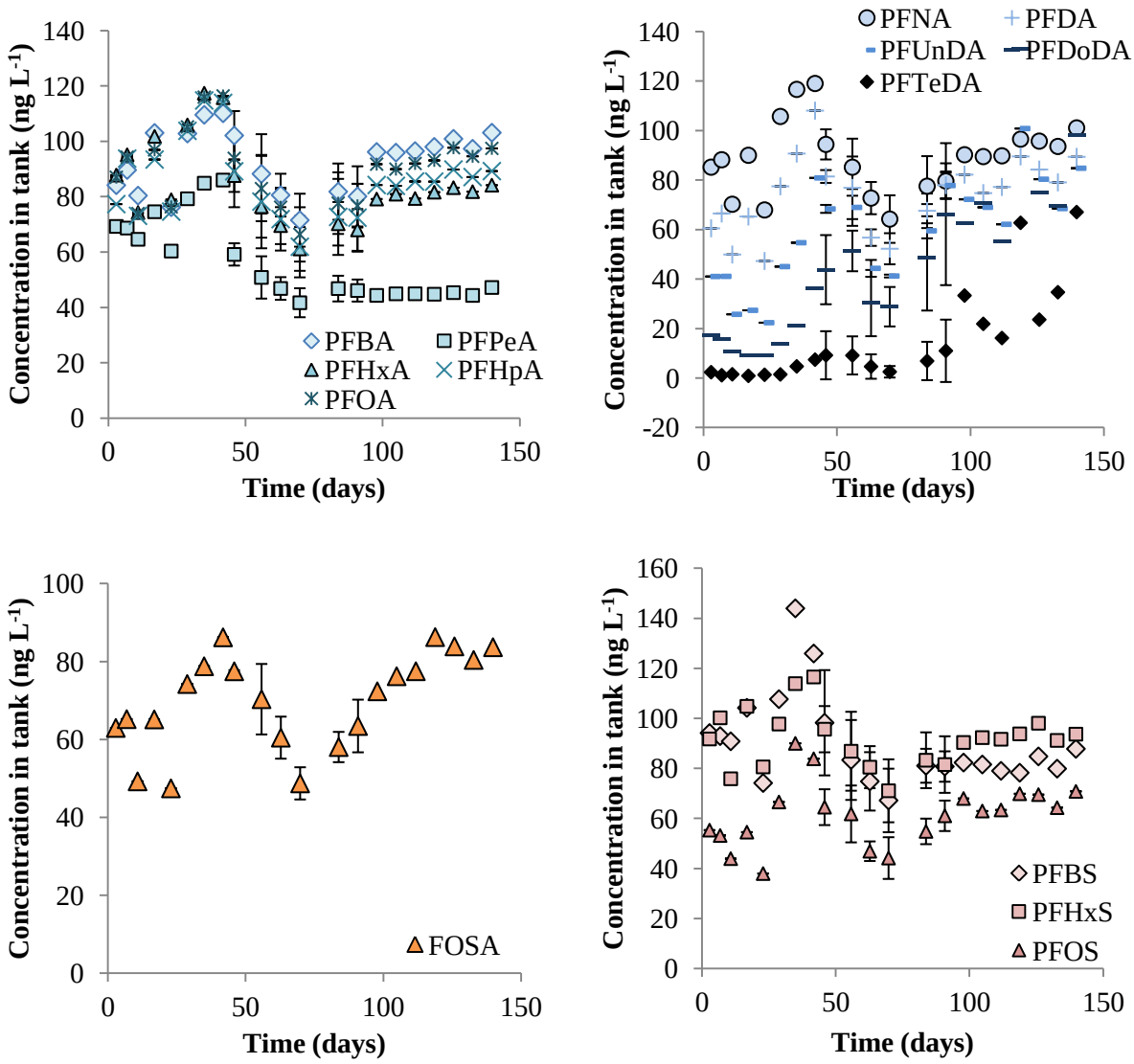

Figure A1. The concentration of individual PFASs in the reservoir tank during the 140 day experimental period.

Table A3. Average concentration of individual PFASs in the reservoir tank over the 140 day experimental period

Compound name	Average concentration in tank (ng L^{-1})
PFBA	93±11
PFPeA	57±15
PFHxA	85±15
PFHpA	86±14
PFOA	90±13
PFNA	89±14
PFDA	74±15
PFUnDA	59±21
PFDoDA	46±33
PFTeDA	15±19
FOSA	70±12
PFBS	90±18
PFHxS	92±11
PFOS	61±13

Appendix C. Results: pilot-scale column experiments using granular activated carbon and anion exchange

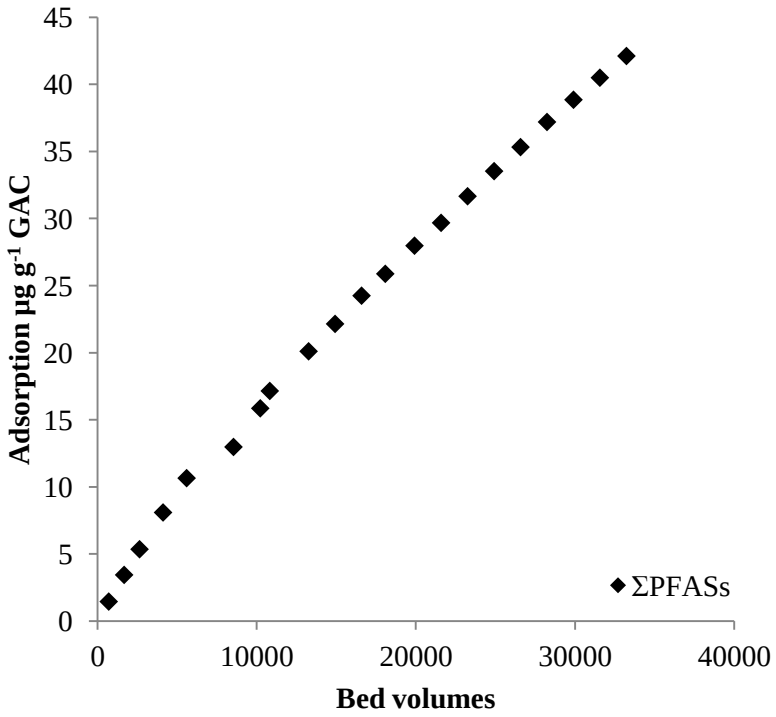

Figure A2. The cumulative concentration for all investigated PFASs (n=14). After 140 days (33 223 BVs), 43.02 *µ*g PFASs g^{-1} GAC was adsorbed.

Table A4. The cumulative adsorption of individual PFASs to GAC during 140 days (33 223 BVs)

Compound name	Adsorption *µ*g g^{-1} GAC after 140 days (33 223 BVs)
PFBA	0.98
PFPeA	0.30
PFHxA	2.95
PFHpA	3.50
PFOA	4.34
PFNA	4.66
PFDA	4.03
PFUnDA	3.31
PFDoDA	2.58
PFTeDA	0.89
FOSA	4.08
PFBS	3.12
PFHxS	4.66
PFOS	3.62
Total	43.02

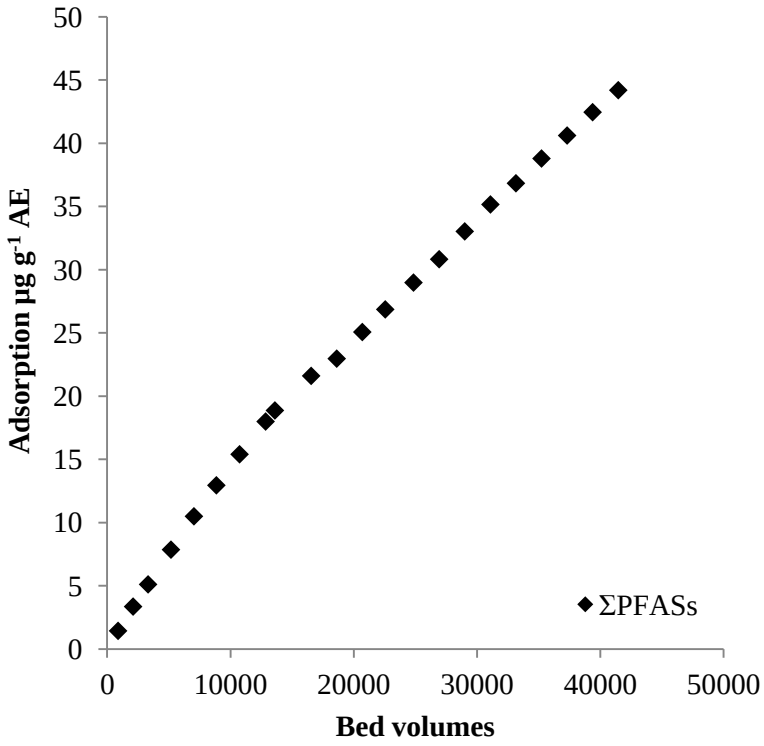

Figure A3. The cumulative adsorption for all investigated PFASs (n=14). After 140 days (41 452 BVs), 45.07 *µ*g PFASs g^{-1} AE was adsorbed.

Table A5. The cumulative adsorption of individual PFASs to AE during 140 days (41 452 BVs)

Compound name	**Adsorption *µ*g g^{-1} AE resin after 140 days (41 452 BVs)**
PFBA	0.45
PFPeA	-1.42
PFHxA	1.51
PFHpA	3.07
PFOA	4.57
PFNA	5.26
PFDA	4.68
PFUnDA	3.89
PFDoDA	2.98
PFTeDA	0.90
FOSA	4.48
PFBS	4.46
PFHxS	5.98
PFOS	4.26
Total	45.07

Appendix D. Methodology: Results from pretests determining amount of granular activated carbon and anion exchange

Amount of GAC or AE used in laboratory batch experiments was determined by performing a pretest. In the pretest, five different amounts of GAC was added to beakers containing the two water types and experiments were performed as described in section 3.3 (batch experiments at SLU). The purpose of the pretest was to determine which amount of GAC would lead to an approximately 50% reduction in DOC, i.e. the DOC reduction should not be too large, otherwise the remaining amount might not be detectable and the DOC reduction should not either be too small, otherwise no difference between the treatments would be detectable. Pretests were performed on DOC and not PFASs due to that PFAS analysis is time consuming.

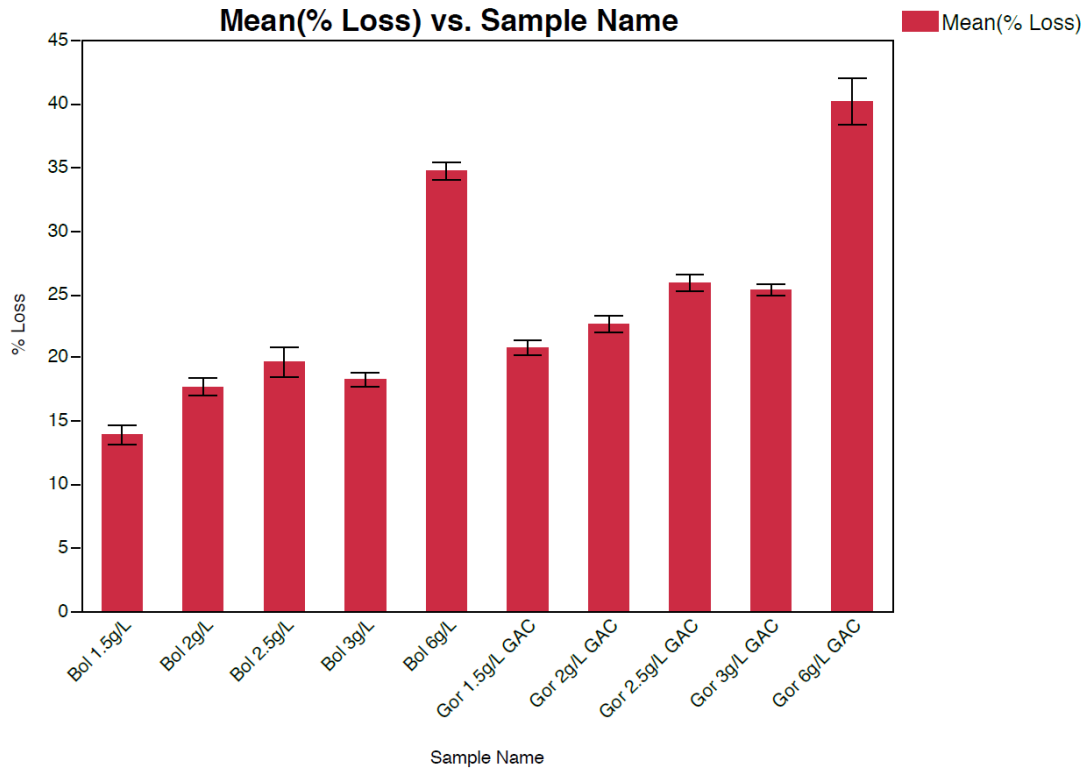

Figure A4. Results from the pretests using GAC concentrations 1.5, 2, 2.5, 3 and 6 g L^{-1} in both water types (BOL = lake Bolmen and GOR = lake Görväln). % loss is the reduction in DOC concentration during the treatment.

Appendix E. Methodology: Experimental set up of pilot-scale column experiments

Figure A5. Experimental set up of pilot-scale experiment at Bäcklösa drinking water treatment plant.

Appendix F. Methodology: Experimental set up of laboratory batch experiments

Figure A6. Experimental set up of laboratory batch experiments.

Appendix G. Methodology: Solid phase extraction

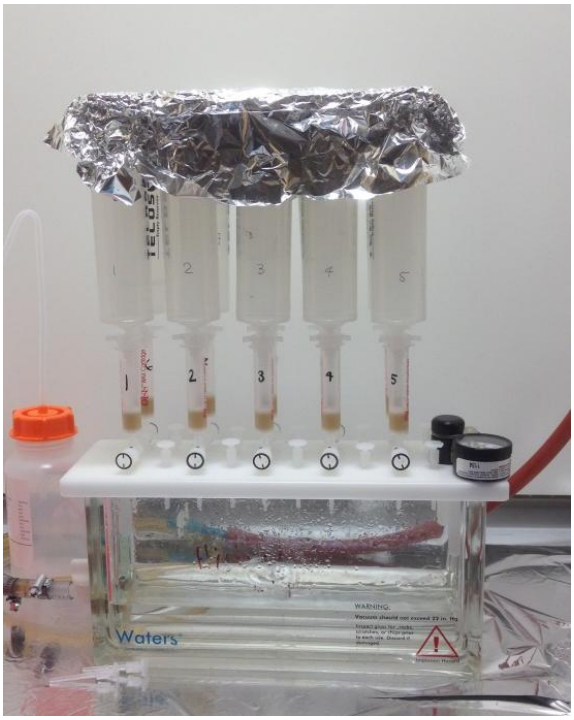

Figure A7. Solid phase extraction (SPE) set up for sample analysis.